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Solar thermal reforming of methane feedstocks for hydrogen and syngas production—A review

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A B S T R A C T

It is currently accepted that at least for a transition period, solar-aided reforming of methane-containing gaseous feedstocks with natural gas (NG) being the first choice, can offer a viable route for fossil fuel decarbonization and create a transition path towards a "solar hydrogen- solar fuels" economy. Both industrially established traditional reforming concepts, steam and dry/carbon dioxide reforming, being highly endothermic can be rendered solar-aided and thus offer in principle a real possibility to lower the cost for introducing renewable hydrogen production technologies to the market by a combination of fossil fuels and solar energy. They also share similar technical issues considering linking of their key thermochemistry and thermodynamics to efficient exploitation of solar energy. In this perspective, the current article presents the development and current status of solar-aided reforming of gaseous methane-containing feedstocks, focussing in particular on the reactor technologies and concepts employed so far to couple the heat requirements of the methane reforming process to the underlying principles, intricacies and peculiarities of concentrated solar power (CSP) exploitation. A thorough literature review is presented, addressing practically the whole scale of solar reactors employed so far: from small-scale reactor prototypes often tested under simulated solar irradiation up to scaled-up reformer reactors tested on solar platform sites at the level of few hundreds of kilowatts. Having presented the current state-of-the-art of the technology, topics for future work are suggested and issues to help further commercialization are addressed.

Contents

1. Introduction

Hydrogen (H_2) has a long tradition as an energy carrier and as an important "raw material" in chemical industries and refineries. Hydrogen can be produced from a variety of feedstocks, gaseous, liquid and solid, including fossil fuels such as natural gas, oil and coal respectively, as well as renewable such as biomass and

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water [1]. Virtually all hydrogen produced today is sourced from fossil fuels, with the principal method employed being the catalytic reforming of methane (CH_4, the principal component of natural gas and other gaseous fuels such as landfill or coal seam gas). Two different reactions can be distinguished in the methane reforming process: steam methane reforming (SMR) and CO_2 (or dry) methane reforming (DMR), represented by the following Eqs. (1) and (2), respectively:

$$CH_4 + H_2O \leftrightarrows 3H_2 + CO \quad \Delta H^0_{298\ K} = +206\ \text{kJ/mol} \tag{1}$$

$$CH_4 + CO_2 \leftrightarrows 2H_2 + 2CO \quad \Delta H^0_{298\ K} = +247\ \text{kJ/mol} \tag{2}$$

Both these reactions are highly endothermic, therefore the heating value of the product is greater than the heating value of the reactants and both reactions are favored by high temperatures (industrial reforming processes are carried out between 800 and 1000 °C) [1]. The required energy is supplied by combustion of additional natural gas and process waste gas (tail gas) from the downstream hydrogen purification step. The share of natural gas, consumed as fuel, varies from 3% to 20% of the total natural gas consumption of the plant, depending on the subsequent energy requirements of downstream processes (e.g. CO_2 removal) [2]. The reaction gas product mixture is known with the name Synthesis Gas (syngas). Syngas is a gas mixture that contains varying amounts of CO and H_2 whose exothermic conversion to fuel and other products has been commercially practiced since a long time ago e.g. via the Fischer–Tropsch technology and which can be also used as a source of pure hydrogen and carbon monoxide [3,4]. In fact Hydrogen and syngas are the basic raw materials to produce synthetic liquid fuels (SLF) and chemicals via industrially available processes.

There are additional ways to produce hydrogen and/or syngas; e.g. from biomass processing, coal gasification, other hydrocarbons, etc. Whilst reforming is likely to remain the technology of choice for some time, hydrogen is ultimately seen to be the clean fuel of the future and will need to be produced entirely from renewable or carbon-neutral energy i.e. with energy input from sunlight, wind, hydropower or nuclear energy [5]. In this perspective, the harnessing of the huge energy potential of solar radiation and its effective conversion to hydrogen becomes a subject of primary technological interest. There are basically three pathways for producing Hydrogen with the aid of solar energy [6,7]: electrochemical, photochemical and thermochemical. The latter is based on the use of concentrated solar power (CSP) radiation as the energy source for performing high-temperature reactions that produce Hydrogen – in many cases first via syngas – from transformation of various fossil and non-fossil fuels via different routes such as water splitting (to produce

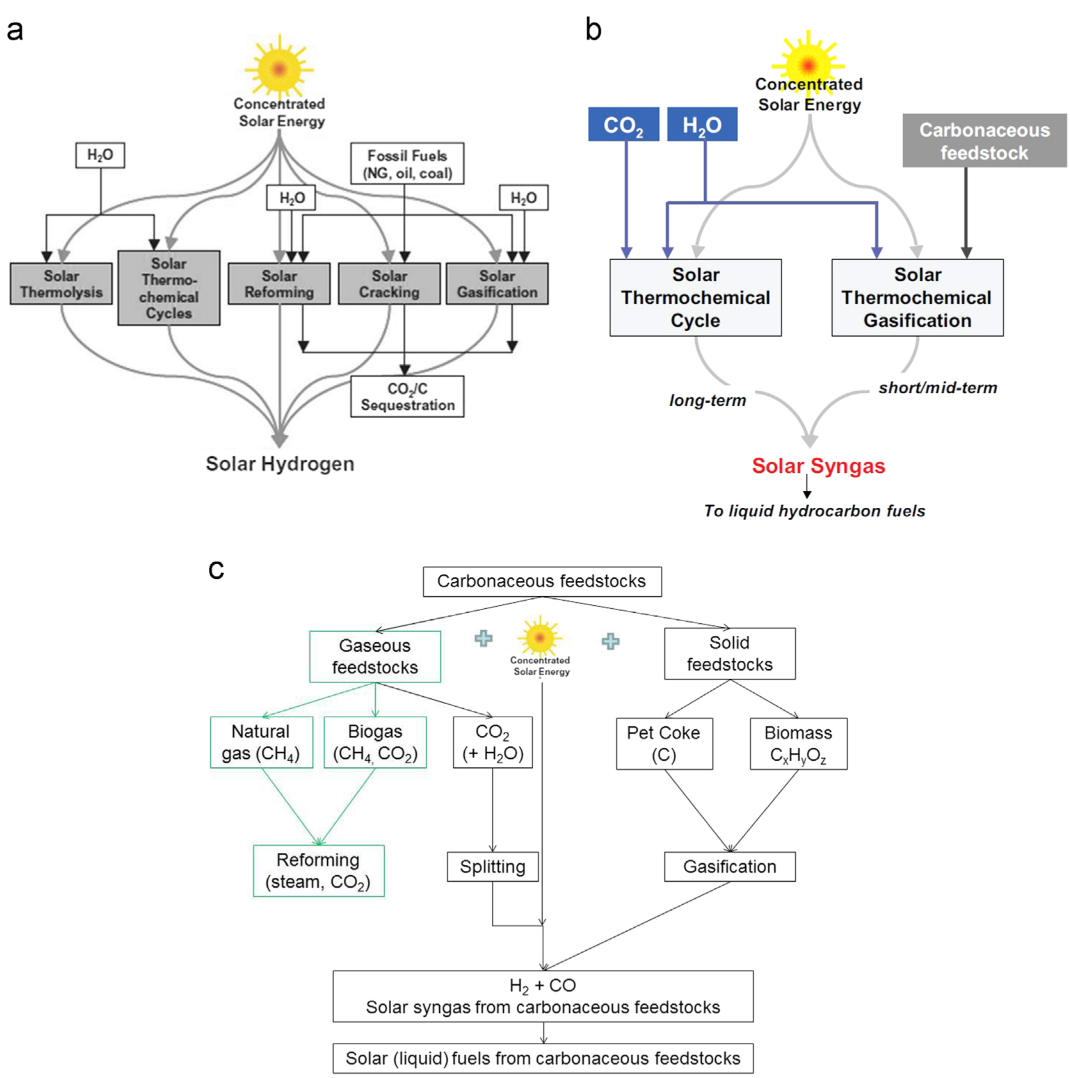


Fig. 1. CSP-aided routes for the production of (a) "solar hydrogen" [6]; (b) "solar syngas" [22]; (c) technologies and raw materials for the production of "solar syngas" from carbonaceous feedstocks (in green: topics covered in this work). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

hydrogen and oxygen) [8–10], natural gas steam reforming (to produce syngas) [11–13], natural gas cracking (to produce hydrogen and carbon black nanoparticles) [14–17] and gasification of solid carbonaceous materials like coal or biomass (to produce syngas) [18–20]. All of these routes involve in some step endothermic reactions that can make use of concentrated solar radiation as their energy source of high-temperature process heat. When solar energy is employed as the energy source for the production of the raw materials for the synthesis of fuels, the latter are characterized with the term "solar fuels". In the broad sense this term can contain in addition to "solar hydrogen", synthetic liquid hydrocarbons and alcohols that are produced from reactions between H_2 and CO that have originated from solar-aided dissociation processes (depicted in Fig. 1) as well as metal powders that can be obtained by solar thermal reduction of metal oxides [21]. The various CSP-aided "solar hydrogen" production routes are shown schematically in Fig. 1a [6] and those for "solar syngas" in Fig. 1b [22]. A further elaboration of the latter case, showing in greater detail the various raw materials and routes for CSP-aided production of "solar syngas" is depicted in Fig. 1c.

Obviously, the ideal raw material for Hydrogen production is water, due to its abundance, low price and the absence of CO_2 emissions during its dissociation to hydrogen and oxygen. However, its single-step thermal dissociation (known as water thermolysis—Fig. 1a), although conceptually simple, requires temperatures in excess of 2200 °C for obtaining some significant dissociation degree [8]. On the other hand solar-aided water splitting by thermochemical cycles – a series of chemical steps by which the net result is the splitting of water into hydrogen and oxygen at lower temperatures – even though demonstrated experimentally on a pilot-solar-plant level [23], still has to resolve some technical barriers to reach full technical maturity for large scale implementation.

Therefore, at least for a transition period, hydrogen supply at a competitive cost can only be achieved from hydrocarbons—essentially natural gas (whose principal component is methane) using well-known commercial processes like steam reforming where methane and steam are converted to syngas. As an intermediate step, considerable effort is being spent on developing a hybrid hydrogen technology in which concentrated solar thermal energy is used to provide the heat for the high temperature endothermic steam–methane reforming reaction. In doing so, solar energy is embodied thermochemically in the product hydrogen. This overcomes many of the limitations of solar energy, enabling it to be stored at ambient conditions, transported from the point of collection to where it is required and enabling it to be used outside daylight hours. Such a transitional technology is considered by many to be an essential stepping stone from current practice to a truly renewable-based hydrogen economy [21,24].

Another promising application for solar reforming is the exploitation of remote natural gas resources, with high carbon-dioxide content. These sources can usually not be exploited economically as conventional natural gas resources, due to high costs for purification and transport. Since solar dry- or mixed-reforming (reaction of the natural gas source with a mixture of water and CO_2) of these natural gas resources yields a syngas appropriate for further conversion into liquid fuels, this states an attractive possibility for future exploitation of these resources. These liquid fuels can easily be transported and utilized as transportation fuel in of energy demanding regions of the world (e.g. Europe or Japan). The most promising liquid fuels to be generated from solar syngas are methanol, dimethyl ether (DME) and Fischer–Tropsch diesel. For the described application Fischer–Tropsch diesel has two major advantages: It has the highest volumetric energy density of these fuels (which is advantageous for ocean transport) and it can be processed and utilized as pure or blend-in fuel without modification to either fuel distribution equipment or engines [25]. The major disadvantage of Fischer–Tropsch Diesel in this context is the low selectivity towards diesel: in Fischer–Tropsch synthesis a variety of hydrocarbons is produced and complex measures have to be taken to increase the yield of diesel fuel [26,27]. DME is, in commercial production plants produced via further processing of methanol, though a number of single step processes for direct production of DME from syngas are being developed. DME can easily be distributed utilizing LPG infrastructure and can be utilized in combustion engines as diesel substitute without modification to the engine itself. Modifications are necessary to the fuel delivery system, such as pumps and injector. A major advantage of DME compared to methanol is, that it is considered environmentally benign and relatively harmless considering health concerns [28]. Methanol can be used as a blend-in fuel in conventional fuels, for example as M85 (85% methanol, 15% unleaded gasoline) with minor modifications to the engine. Though, a major prospect for broad utilization of methanol is the development of the direct methanol fuel cell (DMFC) to a commercial status for utilization in transportation and substitute for batteries in mobile applications, such as mobile phones and laptop computers [29]. Furthermore methanol can be utilized as fuel for PEM fuel cells with previous on-board reforming to hydrogen [29,30]. This possibility has the advantage of easier transport and handling of the fuel, compared to the utilization of pure hydrogen. For all three of these liquid fuels, there is a broad range of applications with minor barriers to overcome, regarding the utilization. On the other hand, the production coupled to a solar reforming plant has not been realized yet and the intermittent character of solar energy supply makes a direct adoption of conventional steady-state process layouts difficult. Therefore the main task to do before being able to commercialize the production of liquid fuels via solar reforming of natural gas is a thorough investigation of the dynamic behaviour of the associated production process.

Methane is the most abundant hydrocarbon and it also has the highest hydrogen content. Water is also rich in hydrogen and therefore the steam/methane reforming reaction is the preferred reaction for hydrogen production. However, in addition to natural gas, there are plenty of other promising methane-containing gases for hydrogen production, e.g. in refineries and steel production plants such as coke oven gas, refinery gas and biogas, with their composition, though, varying notably depending on their source. Coke is an essential input to the iron-making process and is produced by heating coal in coke ovens. Coke oven gas is generated as a by-product of the process and it consists among others hydrogen, methane and carbon monoxide. Refinery gas is defined as non-condensable gas obtained during distillation of

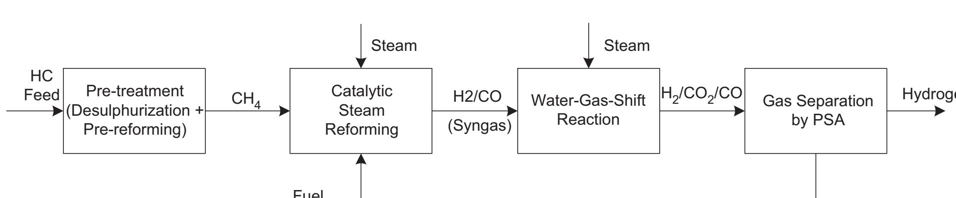


Fig. 2. Block diagram showing the key processing steps in the production of pure hydrogen from reforming [31].

crude oil in refineries. Mainly it consists of hydrogen, methane and ethane. Landfill gas or biogas is a product of the anaerobic digestion or fermentation of biodegradable materials, comprised primarily of methane and carbon dioxide (around 50/50%) [31]. Given the fact that carbon dioxide is a by-product of many industrial processes and available for utilization at relatively high temperature – for instance emitted from power plants – CO_2 methane reforming of gaseous feedstocks containing already high levels of CO_2 may be the most effective way in utilizing these two greenhouse gases [32].

Based on the above, the present review outlines the reforming process for hydrogen production, summarizes the key thermochemistry and thermodynamics of the steam–methane reaction, reviews the past and current work being done to integrate solar thermal energy into the steam reforming process and identifies where future work on this topic should be focused. However, considerable work has and is being conducted on using solar thermal energy to drive the CO_2–methane reforming reaction. Since the latter reaction has similar equilibrium and thermodynamic characteristics to those of steam reforming, the challenges of linking these two reactions to solar energy are essentially the same and therefore, for completeness, both solar-driven steam and CO_2 reforming processes are discussed in this article (Fig. 1c).

2. Hydrogen production via reforming of methane feedstocks

2.1. Thermochemistry and thermodynamics of reforming

Actually, the key reforming reaction is only one step in a process that consists of a number of steps depending on the feed gas and on the product requirements. The key steps in the production of pure hydrogen from methane are shown in Fig. 2 [31] and are briefly discussed following the process sequence below.

Feed gas purification/pre-treatment is necessary since the reforming process requires the removal of certain contaminants from the feed gas stream to avoid poisoning of the catalyst. The primary concern here is the removal of essentially all sulphur containing compounds (the type and concentration of which are uncertain and variable) to a concentration preferably below the detection limit of a few ppb. The typical process concept for desulphurisation of natural gas and similar feedstock used industrially for decades is a two-step process: catalytic transformation, followed by adsorption. The catalytic-adsorption approach most often used is hydro-desulphurization (HDS) where hydrogen added to the fuel reacts with organic sulphur compounds (like triophene or tetrahydrothiophene) to form H_2S. The process uses a HDS catalyst, typically $Ni–Mo/Al_2O_3$ or $Co–Mo/Al_2O_3$ and is followed by subsequent adsorption/absorption of H_2S by passing the feed gas through packed beds containing a suitable sorbent such as ZnO or activated carbon at a temperature of 300–400 °C [33]. In some cases, there may also be a large amount of CO_2 in the feed gas, for example when the feed gas is taken directly from a well or from a landfill. CO_2 removal in these cases is typically effected by Pressure Swing Absorption (PSA) using a zeolite bed. PSA is a cyclic process which utilizes the preferential absorption of CO_2 at high pressure to remove it from the gas stream. The zeolite bed is regenerated by allowing the CO_2 to desorb at lower pressures [24].

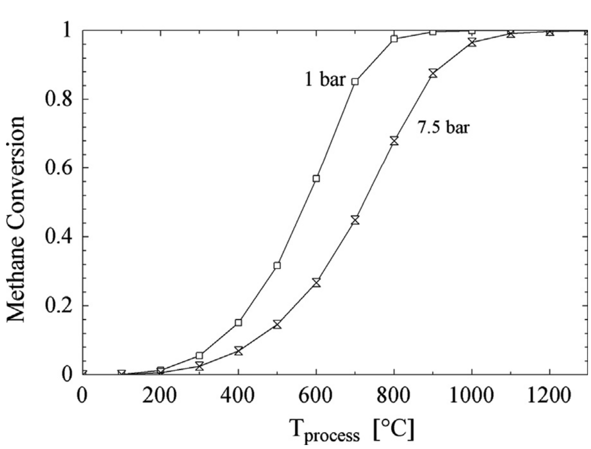


Fig. 3. Conversion of methane in steam reforming as a function of temperature for different pressure levels.

The kinetics and thermodynamics of the reforming reactions are discussed in greater detail below. Both reforming reactions (1) and (2), due to their increase in moles, are favored by low pressures. As can be seen in Fig. 3 methane conversion for a steam reforming reaction reaches 100% around 850 °C at 1 bar, whereas at 7.5 bar the temperature has to be increased to 1200 °C to reach the same conversion. However, commercial reforming plants are operated at much higher pressure levels (usually above 25 atm) [1]. This is due to process optimization: syngas is merely an intermediate product and is further processed (e.g. to hydrogen for ammonia production or to methanol). These consequent processes require high pressures. Heat transfer and mass flow requirements favor high pressures for the reaction as well. Therefore the operation of reforming reactors at the pressure required for the consequent process seems to be the reasonable choice. If higher hydrocarbons (liquid or solid) are in the feed material, pre-reforming is usually carried out (upstream of the main reformer) to convert hydrocarbon feedstocks to CH_4 with the same catalyst but at a low temperature range, typically from 400 to 550 °C. The higher hydrocarbons are converted directly into C_1-components (methane and carbon oxides) with no intermediate products by the steam reforming reactions [34].

In presence of water the reforming reaction is followed by the water–gas-shift (WGS) reaction according to Eq. (3). The WGS reaction is a mildly exothermic reaction in which steam reacts with carbon monoxide to produce hydrogen and carbon dioxide (the same number of molecules on both sides); therefore is favoured by low temperature but is independent of pressure. The reaction is also favoured by a high steam/CO ratio. Although the WGS reaction occurs to some extent in the reforming reactor, it is driven essentially to completion in two separate reaction stages, in fixed-bed catalytic reactors with inter-stage cooling, consisting of a high temperature shift at 350–420 °C involving iron/chromium catalyst and a low temperature shift at around 200–250 °C involving copper/zinc catalyst respectively. However, equilibrium considerations mean that there will always be some CO present.

$$CO + H_2O \leftrightharpoons H_2 + CO_2 \quad \Delta H^0_{298\ K} = -41\ \text{kJ/mol} \tag{3}$$

The overall reaction of steam reforming followed by the WGS is given in Eq. (4):

$$CH_4 + 2H_2O \leftrightharpoons 4H_2 + CO_2 \quad \Delta H^0_{298\ K} = +165\ \text{kJ/mol} \tag{4}$$

As can be seen from reactions (1) and (2) the H_2/CO ratio in the product can differ significantly between 3 and 1 respectively. Therefore in order to provide a high hydrogen yield, steam reforming followed by WGS is most suitable, as a H_2/CO ratio of up to 4 can be achieved. However, the required properties of syngas depend on its subsequent utilization [30], since for further processing to liquid fuels for instance, a molar ratio of H_2/CO above 3 is unsuitable [35,36].

Both reforming reactions can generally be catalyzed by metals of the VIII group of the periodic system. Current state-of-the-art catalytic systems for natural gas steam-reforming are based either on highly expensive precious metals such as Ru and Rh or on systems of significantly lower cost based on Nickel (Ni) metal. In commercial applications, Ni-based catalysts supported on mixed oxides of Ca–Al

[37] or Mg–Al [38] of the hexa-aluminates and spinels structures (e.g. $CaAl_6O_{10}$ or $MgAl_2O_4$ respectively) have proved to be most suitable, due to low cost and high catalytic activity. Other catalysts are not preferred due to high costs (noble metals) or technical issues (Fe and Co). The mixed oxide supports are traditionally synthesized by co-firing of the corresponding oxides at high temperatures (> 1600 °C) for extended periods or from wet chemistry routes that also involve sintering of precipitated powders (even though at lower temperatures). This firing is followed by a second calcination step at 500–700 °C under H_2 flow to reduce NiO to "active" Ni.

The two main issues remaining in reformer design utilizing Ni-based catalysts are sulphur compounds in the feed and carbon formation at the catalytically active site. While the first, as mentioned, can usually be eliminated by a hydrogenator followed by a ZnO bed, the latter constitutes a more complicate issue. Carbon formation in reforming reactions occurs mainly due to methane decomposition (pyrolysis) or disproportionation of carbon dioxide according to Eqs. (5) and (6), respectively.

$$CH_4 \rightarrow C + 2H_2 \tag{5}$$

$$2CO \rightarrow C + CO_2 \tag{6}$$

Both reactions (5) and (6) are catalyzed by metals; therefore the risk of carbon formation is high in presence of Ni-based catalysts. As reported [4], at low temperatures, adsorbed hydrocarbons may accumulate on the nickel surface and slowly be transformed into a polymer film ("gum") blocking the nickel surface. At high temperatures, ethylene from the pyrolysis of higher hydrocarbons may lead to pyrolytic coke, which may encapsulate the catalyst pellets. Whisker carbon formed due to the dissociation of adsorbed hydrocarbons or carbon monoxide on the metal surface to give adsorbed carbon atoms which are dissolved in the metal particle, is the principal product of carbon formation in steam reforming. At a given temperature and pressure and for a given hydrocarbon feed, carbon will be formed below a critical steam-to-carbon ratio. This critical steam-to-carbon ratio increases with temperature. Thus in commercial steam reforming plants most commonly the introduction of excess steam into the feed is used for the reduction of carbon formation risk. Usually the steam to carbon ratio S/C is set between 2 and 5 (resulting in an atomic H/C ratio of 8 to 15). Therefore the share of sensible heat in the process is largely increased and the chemical efficiency of the process decreased. As can be seen from Eq. (2), considering that the aim of the process is a complete conversion of methane, the maximum H/C ratio in dry reforming is 2, decreasing with over stoichiometric CO_2 content in feed. Therefore in dry reforming processes noble metals are more commonly used as catalysts, because reforming can be operated at significantly lower H/C ratios without carbon formation. Another possibility for the inhibition of carbon formation is the addition of promoters to the Ni based catalyst (e.g. alkaline earth metal oxides) [1,4,8,39–41].

After the shift reaction, the product gas ("raw synthesis gas") consists mainly of H_2 and CO_2, and some impurities such as unconverted CH_4 and CO. Therefore, the last "process box" in Fig. 2 – purification – is dependent on the gas separation technology employed. Modern steam reforming plants typically use PSA to remove the CO_2 from the product hydrogen; this process also removes any remaining CO and CH_4 to produce 99.99% pure hydrogen. Alternative separation technologies based on solvents, such as amines, for CO_2 absorption require a separate methanation step to remove the CO from the product gas. Here by "methanation" is meant the reverse of the steam reforming reaction where the undesired CO is converted to CH_4 (reaction 7). Just like in the case of reforming though, there are two possible "methanation" reaction schemes referred in the literature, producing in addition to CH_4, H_2O or CO_2 respectively, as follows:

$$3H_2 + CO \Leftrightarrow CH_4 + H_2O\ (g) \tag{7}$$

$$2H_2 + 2CO \Leftrightarrow CH_4 + CO_2\ (g) \tag{8}$$

2.2. Current industrial status

The commercial feedstock of choice for syngas production is natural gas and the most widely used process is steam reforming as discussed briefly above. Steam methane reformers have been built over a wide range of sizes. For large scale chemical processes such as oil refining, steam reformers manufactured by large plant engineering companies are producing hydrogen in the order of 100,000–1000,000 kg hydrogen per day. Steam reforming is conducted usually inside tubes packed with nickel catalyst. Schematics of the operation and representative photographs of typical industrial reformers are shown in Fig. 4 [42]. The outer diameter of the tubes ranges typically from 100 to 150 mm and their length from 10 to 13 m. The tubes are made of high-temperature alloys (e.g. Cr25–Ni20%) and are heated by radiation and convection from burning natural gas or refinery waste fuel gas. Typical inlet temperatures to the catalyst bed are 450–650 °C and product gas leaves the reformer at 800–950 °C depending on the application. Tubular reformers are designed with a variety of tube and burner arrangements. The heater design – either from the top or from the sides (Fig. 4a, left) – and heat supply has to be such that in the one hand the tube wall temperature is high enough for the reforming reaction but in the other hand the tube surface is not overheated. A typical side-fired reformer (Fig. 4a, middle) has over 350 burners. In top-fired reformers (Fig. 4a, right) the tubes are spaced to allow the down flames to fire between them. The radiant gases leave the box horizontally at the bottom and used to generate the process steam. The capital cost for these large scale steam reformers is in the range of 200 to 400 €/kg H_2.

The process may appear simple from an overall consideration, as the product composition is determined by simple thermodynamics, but in reality it is a complex coupling of catalysis, heat transfer and mechanical design. In commercial applications of methane reforming the activity of the catalyst is usually not the limiting factor. However, heat transfer and diffusion limitations decrease the effectiveness of the catalyst due to the comparably large particle size of the catalyst pellets. In practice, the utilization of the intrinsic catalytic activity as expressed by the effectiveness factor is less than 10% because of transport restrictions; these restrictions have to be taken into account when designing a reformer unit. The effectiveness factor is so low that the activity is roughly proportional to the external surface area of the catalyst. The shape of the catalyst pellet should be optimized to achieve maximum activity with minimum pressure drop. The pressure drop depends strongly on the void fraction of the packed bed and decreases with increasing particle size. Hence, the optimum is a catalyst bed of pellets with large external diameter and with high void fraction, as achieved with rings or cylinders with several holes. Other solutions may be based on the use of catalysts consisting of ceramic foams or monoliths. From intrinsic kinetics it can be shown, that space velocities of $10^4\ h^{-1}$ lead to close-to-equilibrium composition in product gas [1,4,43].

The steam reforming process as practiced today faces a number of constraints. First, thermodynamics demands high exit temperatures to achieve high conversions of methane. In contrast, the catalysts are potentially active even at temperatures below 400 °C. Consequently, there have been efforts to circumvent the constraints by the use of a hydrogen-selective membrane installed in the catalyst bed [44] that will be continuously removing hydrogen from the reactant stream, thereby driving the equilibrium toward higher conversion at lower temperature. A low-temperature membrane reformer would be able to use low-temperature heat, a fact crucial to its coupling with solar

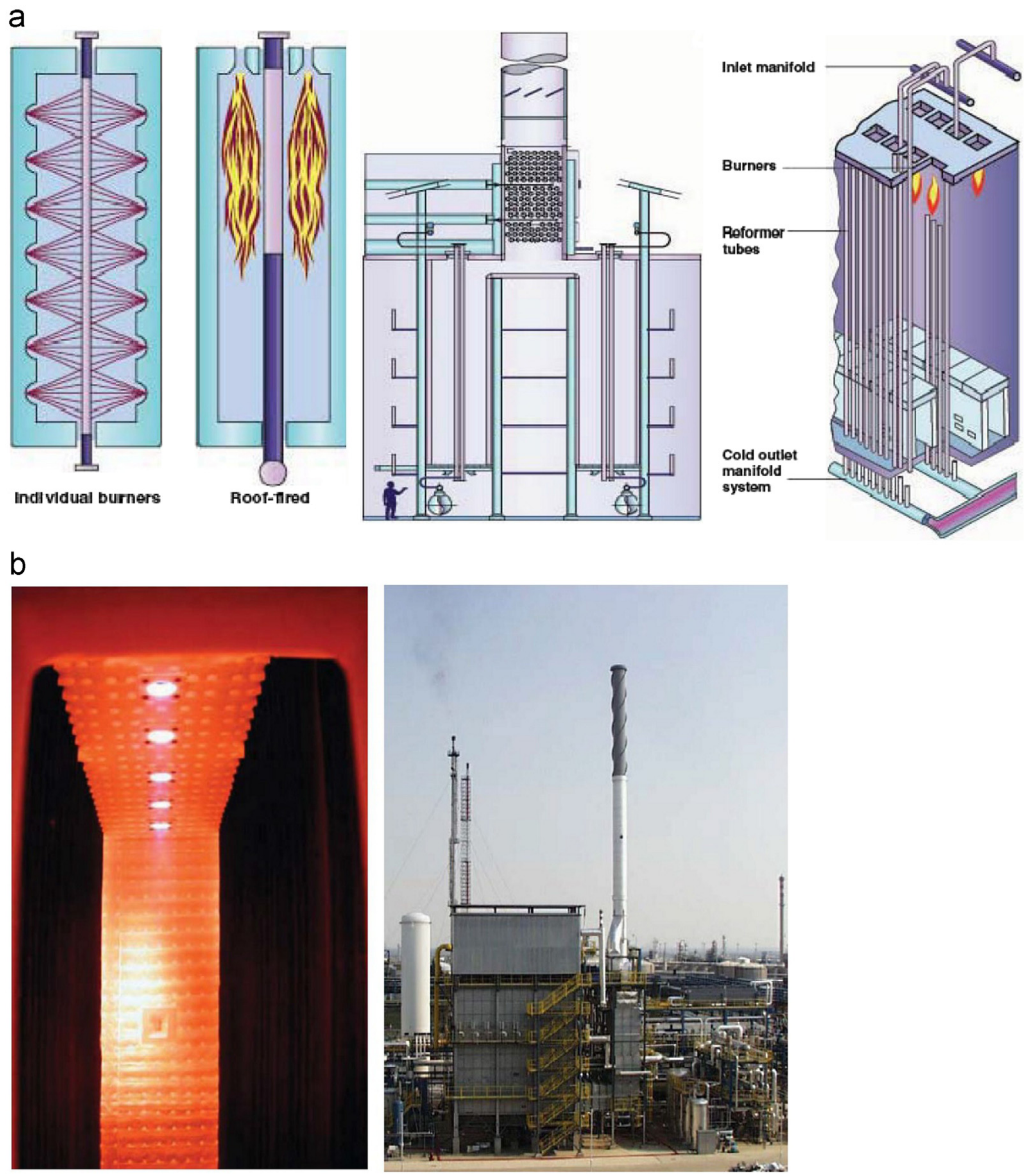


Fig. 4. (a) Schematics of operation and (b) actual photographs of typical industrial reformers [42].

plants as will be discussed below. Reactor simulations and experiments [45] have shown that the reformer exit temperature can indeed be reduced to below 700 °C while the same conversion is maintained. However, the hydrogen produced according to this concept is at low pressure and must be compressed to the usual delivery pressure of 20 bar. This limitation renders the process uneconomical except when very low electricity prices prevail or when hydrogen is used as a feedstock for a fuel cell or as a low-pressure fuel.

In addition (and in contrast) to fired tubular reforming and heat exchange reforming shown in Fig. 4, where the heat is supplied by heat exchange from an external source, current industrial state-of-the-art reforming involves also the so-called adiabatic oxidative reforming concepts where the heat for the reforming reactions is supplied internally by combustion of part of the reactants. The overall reaction is adiabatic, meaning that there is no exchange of heat with the surroundings (except a very limited heat loss). For production of synthesis gas the previously mentioned reactions (1) and (2) are not used; instead a sub-stoichiometric amount of oxygen is added which will thus be all consumed because this is the limiting reactant. It should be noted that the combustion reactions are all irreversible. Two variants are implemented known as partial oxidation (non-catalytic = POX, catalytic = CPO) and autothermal reforming (ATR), depending on the required or desired syngas composition for the downstream processing. In general ATR and POX lead to lower H_2/CO ratios in the syngas, compared to SR with consequent WGS. In POX the feedstock is oxidized partially by pure oxygen, as displayed in Eq. (9).

$$CH_4 + \frac{1}{2}O_2 = CO + 2H_2 \quad \Delta H_{298}{}^{\circ} = -38 \ \text{kJ/mol} \tag{9}$$

Autothermal reforming is really a hybrid of SR and POX, consisting of the reactions displayed in Eqs. (1), (3) and (9) as well as (9a) [1,26,46]:

$$CH_4 + \frac{3}{2}O_2 = CO + 2H_2O \quad \Delta H_{298}{}^{\circ} = -520 \ \text{kj/mol} \tag{9a}$$

One major drawback of these two process variants is the large cost related to the air separation unit that can account for up to 40% of the total cost of the syngas plant [4]. These variants are

mainly attractive for large scale Fischer–Tropsch or Methanol synthesis plants [26].

3. Solar-aided reforming

3.1. Solar concentration systems

Large-scale concentration of solar energy is accomplished at pilot and commercial CSP plants with four kinds of optical configuration systems using movable reflectors (mirrors) that track the sun, namely [47]: parabolic trough (PT) collectors, linear Fresnel (LF) reflector systems, dish–engine (DE) systems and power towers—also known as central receiver (CR) systems (Fig. 5). These systems have been proven to be technically feasible in large-scale (MW) pilot and commercial solar thermal power plants (STPP) aimed at the production of electricity from the sun's rays: the solar energy is concentrated on a focal point by means of movable sun-tracking mirrors providing thus medium-to-high temperature heat. The high-quality thermal energy obtained in this way needs to be converted efficiently to mechanical work. For this purpose, a heat exchanger (receiver) is used, located in the concentration field of the radiation, in which a heat transfer fluid (air, water, saturated or superheated steam, thermal oil, or molten salt) is first solar-heated and then transfers its enthalpy to the production of steam further used in traditional energy cycles (Rankine, Brayton or Stirling) [48]. The temperature that the heat transfer fluid can reach depends on the operating principles of each CSP system and in particular to its capability for solar concentration.

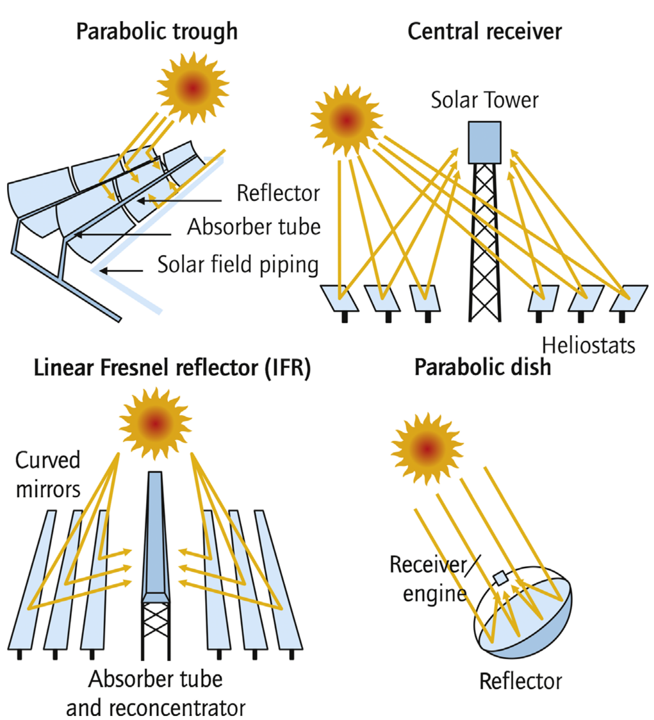


Fig. 5. Schematics of the four solar concentrating technologies currently applied at commercial CSP plants [47].

On the other hand concentrated solar power can be used to provide high-temperature process heat as the necessary energy source for the performance of endothermic chemical reactions in the so-called solar thermochemical processes. Solar thermochemical applications, although not as far developed as solar thermal electricity generation, employ the same solar concentrating technologies but instead of being targeted to power generation, the concentrated solar radiation is focused on an integrated receiver/reactor where endothermic chemical reactions are performed targeted to the production of useful chemicals.

Parabolic trough and Linear Fresnel technologies currently operate at moderate solar concentration ratios with thermal oil or water–steam at working temperatures usually below 500 °C. Thus, regardless of the type of reforming reactor and catalyst, the higher temperatures required for steam or CO_2 methane reforming processes effectively limit the solar concentrator choice to the two types of high-solar-concentration ones namely, the parabolic dish collector and the central tower receiver.

3.2. Coupling reforming with solar energy: Solar receiver–reactor concepts

Both the steam reforming reaction (1) and the CO_2 reforming reaction (2) are highly endothermic and therefore offer an opportunity to embed and thus store solar energy. If solar energy is used to provide the heats of reaction for reactions (1) and (2), in the one hand, a reduction of fossil fuel consumption is achieved because by this way fossil fuels are not used to generate high temperature, instead they are only used as a feedstock. On the other hand, the product gas will contain 26 and 31% of solar energy embodied in chemical form respectively (low heating value basis, assuming water stays as a vapour). As already mentioned, in presence of water the reforming reaction is followed by the water–gas-shift (WGS) reaction according to Eq. (3). Because the WGS reaction is exothermic, the conversion of CO to hydrogen and CO_2 actually reduces the amount of energy that can be stored in the products, to 21% in both cases (since in both cases 4 mol of H_2 are produced per mole of methane) [24].

This storage of solar energy can be further "exploited" via two process options. In the so-called "open-loop" systems, a hydrocarbon feedstock (e.g. natural gas, pyrolyzed or gasified coal or oil shale, or low-quality hydrocarbon gases or waste CO_2-rich natural gas or coal-bed methane) is upgraded in energy content with solar energy (Fig. 6a) to produce directly on-site H_2/CO "solarized" fuel syngas for subsequent combustion in a conventional gas turbine (GT) or a combined cycle (CC) power plant. This "solar-boosted" fuel could simply be supplied to the power plant only during daylight hours, or gas storage could be included for 24 h/day operation of the GT-CC plant [49]. These concepts are more

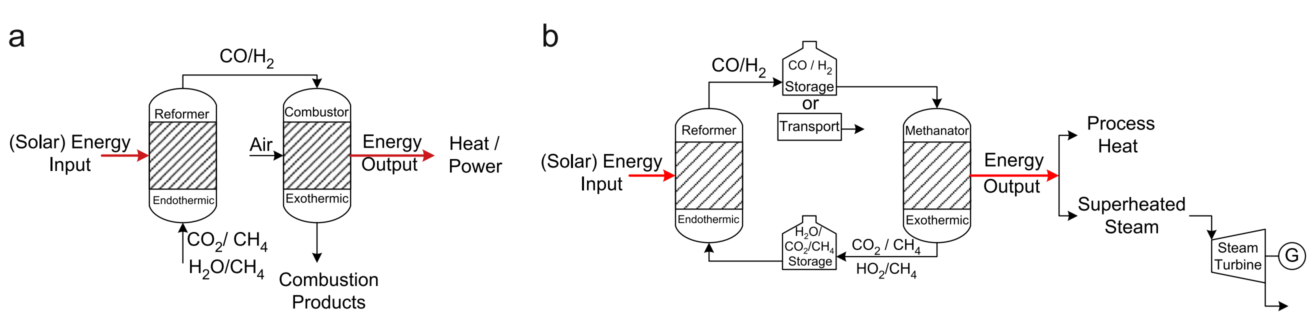


Fig. 6. Concepts for (a) closed and (b) open loop thermochemical heat pipes based on CH_4/CO_2 reforming and solar energy (adapted from [51]).

thermally efficient than simply using the solar energy to produce steam because they harvest the solar energy in chemical form, rather than in sensible heat; thus the solar energy share in the product fuel can be converted to electricity at significantly higher efficiencies in large GTCC plants (at 45–50% thermal efficiency) rather than just using it in the less efficient steam turbine (ST) cycle (at 30–35% thermal efficiency) [50,51]. Additional potential utilization of the product syngas is directed to fuel cells (FC), for further processing to specialty chemicals and plastics and liquid fuels (methanol and gasoline).

In the so-called "closed-loop" systems, a high-quality hydrocarbon feedstock such as methane (CH_4) is converted to syngas via

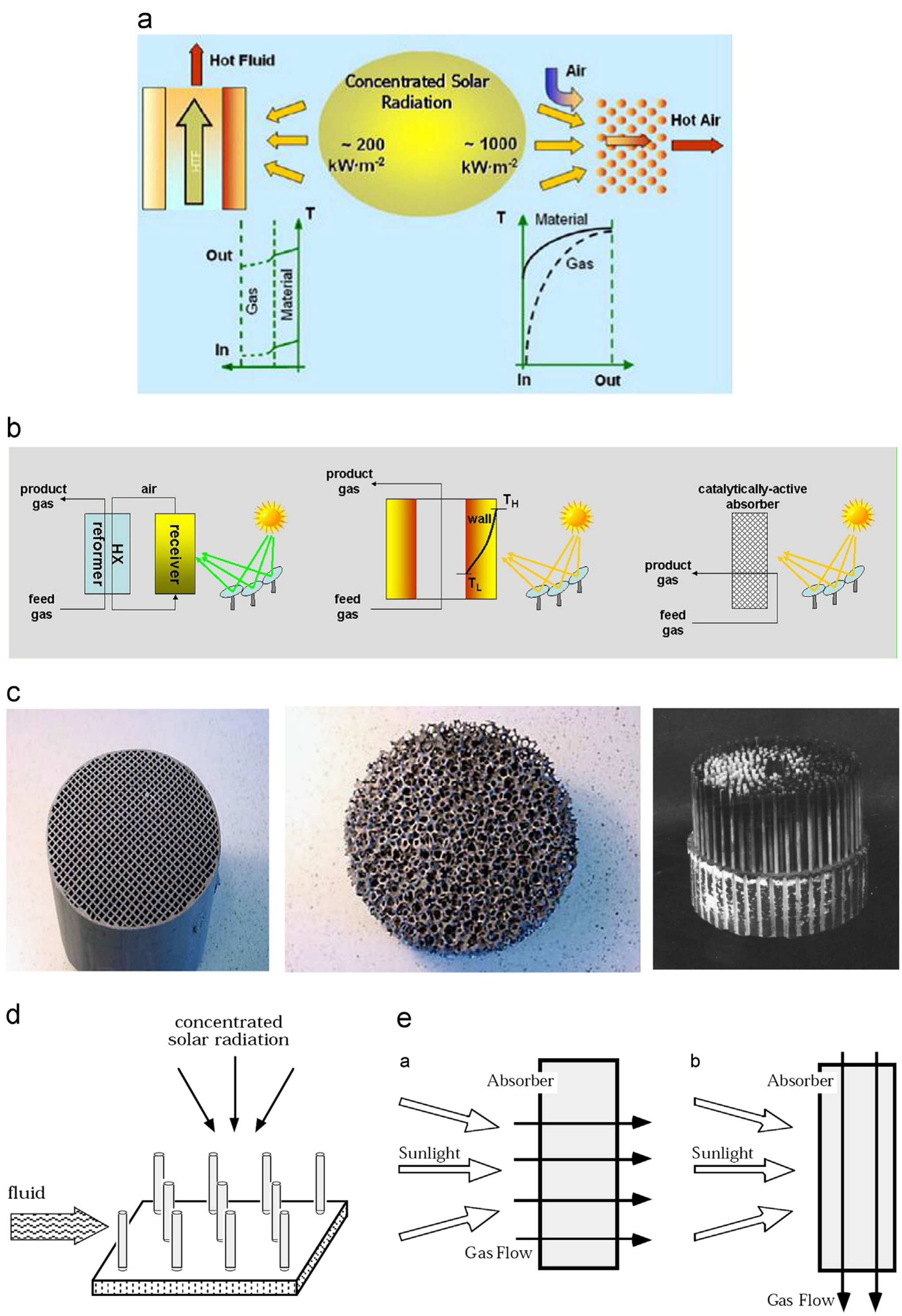


Fig. 7. (a) Operational principles of indirectly heated tubular (left) and directly heated volumetric (right) solar receivers [61]; (b) operation principles of indirectly-irradiated receiver decoupled from the reformer (left), indirectly irradiated integrated tubular reactor/receiver (middle) and directly irradiated reactor/receiver (right); (c) monolithic ceramic structures explored as volumetric receivers: honeycomb (left), foam (middle) [59] and pin-finned (right); (d) "porcupine" volumetric solar absorber concept; (e) incident radiation and flow directions in volumetric absorbers: incoming sunlight and working-fluid flow are in the same general direction (foam, honeycomb, etc. left), or the flow is perpendicular to the irradiation (porcupine-right) [55].

solar reforming; the syngas is then stored or transported off-site prior to conversion back to CH_4 in a methanation reactor that recovers the solar energy as heat for industrial processes or power generation (Fig. 6b). Closed-loop solar reforming of CH_4 and energy recovery in a methanator has been considered as a method for storage of solar energy that would match the short-term storage requirements of steam-cycle power plants for peaking power generation or provide longer-term storage and/or thermal energy transport over moderate distances to multiple sites for process heat applications (between, for example, high-insolation solar collection sites and major industrial centers) [52]. Both methanation reactions (7) and (8) are exothermic and the energy recovered in the methanator can in principle either be integrated with a conventional steam turbine power plant or be used for the production of high grade process heat. However, because of this reaction exothermicity and in order to obtain high methanation conversion, temperatures must be controlled not to exceed a medium range, otherwise the back reaction (reforming) can take place—a fact that can limit the usage of the steam produced only for process heat and not for power generation. Traditionally, this has been handled by using a high recycle and thus diluting the inlet gas in order to keep the temperature below 450 °C. However, nowadays, there are a number of technology concepts and pilot plants around (e.g. TREMP^{TM} process of Haldor Topsoe) to recover the heat as high-pressure superheated steam at 100 bar g/540 °C that can be incorporated directly in a steam turbine power cycle [53].

For the efficient design and operation of solar receiver/reactors, concepts from "traditional" chemical reactor engineering should be combined with ways to achieve efficient heating of the reactor via concentrated solar irradiation. Just like in the "traditional" non-solar chemical engineering, the catalytic reactor type can be distinguished in two broad categories depending on whether the catalyst particles are distributed randomly or are "arranged" in space at the reactor level: the first category includes packed and fluidized catalytic beds; the second includes the so-called "structured" catalytic systems like honeycomb, foam and membrane catalytic reactors, all three of them being free of randomness at the reactor's level [54].

Solar receivers can be distinguished in two broad categories according to the mechanism of transferring the solar heat to the heat transfer fluid: directly and indirectly heated ones. The common characteristic of the historically precedent indirectly

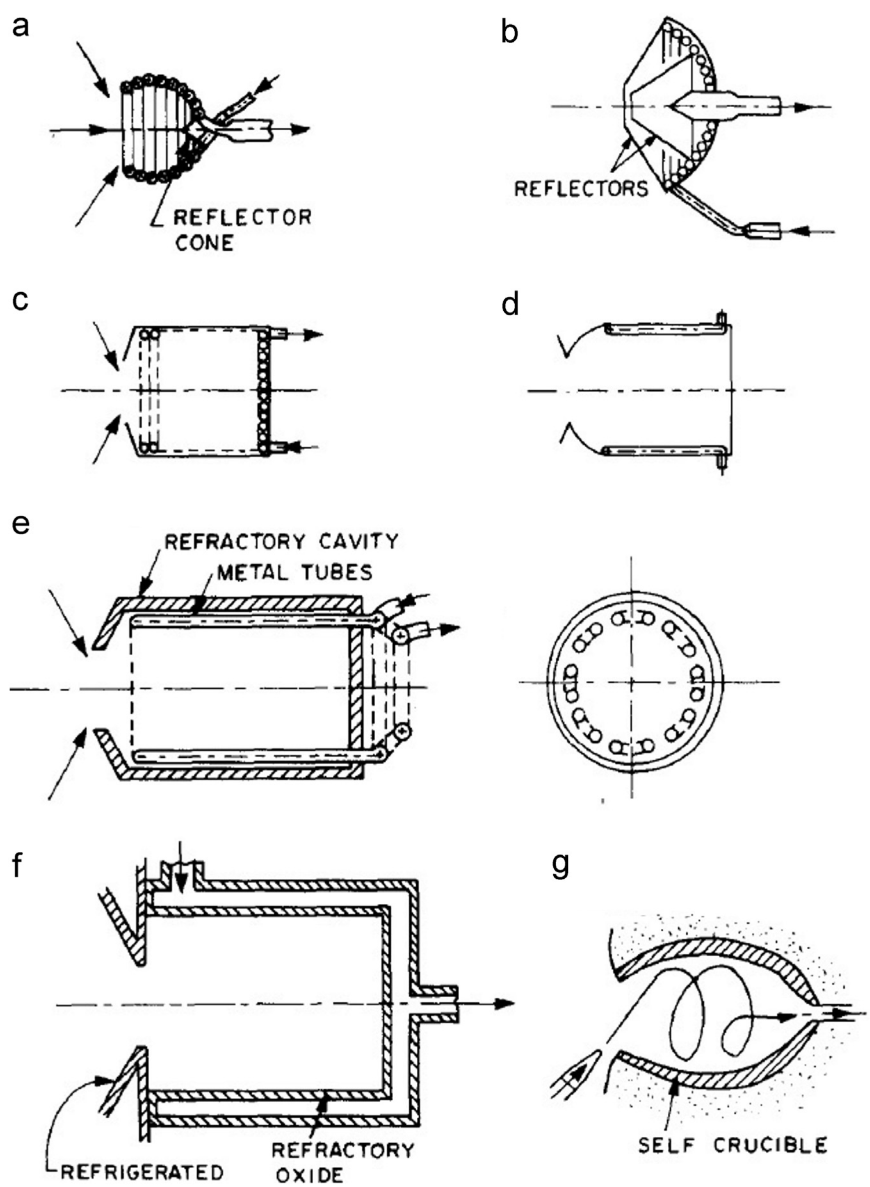


Fig. 8. Various design concepts for solar reactors [56].

irradiated receivers (IIR) is that the heat transfer to the working fluid does not take place upon the surface which is exposed to incoming solar radiation. Instead, there is an intermediate opaque wall, heated by the irradiated sunlight on one side and transferring the heat to a working fluid on the other side [55]. The simplest examples are conventional tubular receivers that consist of absorbing surfaces exposed to the concentrated solar irradiation. The heat transfer fluid (e.g. a gas or a molten salt) is moving in a direction vertical to that of the incident solar radiation (Fig. 7a, left); heat transfer to the thermal fluid takes place through the receiver opaque walls first from the outer to the inner wall surface by conduction and subsequently from the inner tube wall to the heat transfer fluid by forced convection.

In the case of receiver–reactors two further options are possible: in the first option the receiver and the reactor are de-coupled. The latter is not located within the solar absorbing module: the energy of a solar-receiver-heated heat transfer fluid is transferred via insulated tubes to a reactor where endothermic chemical reactions take place (a reactor heated indirectly via this concept is often encountered in the literature as “allothermal”). The operation principle of this concept is shown schematically in Fig. 7b, left. The same de-coupled configuration can be used when an-other-than-solar high-temperature source is available e.g. a chemical reactor can be heated via hot circulated Helium coming from nuclear reactors. Alternatively, the solar-heated tubular receivers can contain the catalyst material in the form of either packed beds or even liquid beds (when a material is solar-heated slightly above its fusion temperature and the reacting gas is injected into the liquid bed [56] in an analogy of the technique employed in gas metallurgy processes with molten metal baths) or, finally, as structured assemblies—again in these cases the catalyst is heated via conduction through the tube walls. The operation principle of this concept is shown schematically in Fig. 7b, middle. A number of design versions of such reactors for solar hydrogen production can be found since 1981 and are reproduced here in Fig. 8. Finally, another version of indirectly heated receivers are the so-called Heat Pipe Receivers where concentrated sunlight is employed for the evaporation of a liquid substance (e.g. liquid sodium) which in turn condenses on the tubes containing the reactant gas, liberating the heat of vaporization which in this case is transferred isothermally to the reactant gas through the walls since evaporation–condensation occurs at a constant temperature [57].

However, the most direct and therefore potentially the most efficient method would involve direct heating of the heat transfer fluid by the concentrated beam, thus eliminating the wall as the light absorber and heat conductor. Directly irradiated receivers (DIR) make use of fluid streams or solid particles directly exposed to the concentrated solar radiation. A key element of all directly irradiated receivers is the absorber: the component which absorbs concentrated sunlight and transports its energy to a working fluid flowing within and over it. Directly irradiated receivers are also called and “volumetric” receivers since they enable the concentrated solar radiation to penetrate and be absorbed within the entire volume of the absorber. In different designs, the absorber is either a stationary matrix (grid, wire-mesh, foam, honeycomb, etc.), or moving (usually solid) particles.

Directly irradiated receivers with stationary absorbers are relatively simple and the most common of the volumetric receiver family. Here, the absorbing matrix must be able to absorb highly concentrated radiation, while providing sufficient heat convection to the working gas flow. It is also required to sustain thermal stresses created by large temperature gradients as well as thermal shock caused by rapid heating–cooling cycles. Such receivers, first proposed in the early 1980s [56,58] are compact heat exchangers comprising of a pack of high-porosity material structures capable of absorbing the concentrated solar radiation and transfer it to a gaseous heat transfer medium [59,60]. For instance, gas (air) can be driven through the absorber, flowing past the absorbing structures parallel to the direction of the incoming radiation (Fig. 7a, right) [61]. Hence, the volumetric receiver concept entails that the solar irradiation and the heat extraction take place on the same surface simultaneously (Fig. 7b, right) which also functions as the reaction surface. In this case the direct heat transfer via radiation upon the receiver/reactor surface is far more efficient than that achieved via convection through the walls of a tubular receiver/reactor. In addition, this direct irradiation evokes the highest temperatures in the system to be located on the absorber′s surface which is simultaneously the site of reaction. Considering the mechanisms mentioned in Section 2.1 this leads to increased conversion compared to other concepts. In the concept of the irradiated reactor tube for instance, the highest temperature is encountered at the outer tube surface and due to the resistance to heat transfer via conduction through the wall, the actual heat flux to the reaction site (inner region of the tube) is much lower. Due to the tube materials temperature limitations, this significantly decreases the reaction temperature. Furthermore, in volumetric receiver–reactors, high energy fluxes can be utilized, due to chemical cooling by the endothermic reaction in addition to sensible cooling by the temperature difference between gas stream and absorber structure. This leads to a smaller absorber area decreasing the total re-radiation losses of the structure, compared to the other technologies, where larger absorber areas are necessary in order to achieve the same syngas production.

Such receiver structures can be steel or ceramic wire meshes [60,62], ceramic foams (Fig. 7c, left)—or multi-channelled honeycombs (Fig. 7c, middle). In fact such structures have been extensively tested in CSP facilities [60,62–65]. Volumetric receivers based on ceramic honeycombs developed in the Deutsche Zentrum fur Luft-und Raumfahrt—German Aerospace Center (DLR), have currently reached the level of commercial exploitation in the 1.5 MWe Solar Tower Julich (STJ) Thermal Power Plant, being capable of heating ambient air to temperatures around 700 °C that is further used in traditional energy cycles supplying power to the local community [66]. Researchers at the Weizmann Institute of Science (WIS), Israel, have introduced and explored an alternative design of a structured volumetric (directly-irradiated) solar absorber, nicknamed “Porcupine”, its schematic view presented in Fig. 7c, right [55]. It is an array of pin-fins, constructed with elongated heat transfer elements made of ceramic tubes or rods (i.e., the porcupine ‘quills’), implanted in a base plate. The cross-flow pattern introduces turbulent mixing and enhances the rate of convective heat transfer from the absorber matrix to the fluid. In all the other stationary absorbers mentioned previously, the flow is in the general direction of the incoming light, as shown schematically in Fig. 4e, left. In the Porcupine the tubular elements are roughly aligned with the irradiation, and the mean flow direction is perpendicular to both (i.e., cross-flow; Fig. 7e right). The latter configuration is claimed to allow better flexibility in the design of the flow inlet and outlet ports. The cross-flow pattern introduces turbulent mixing and enhances the rate of convective heat transfer from the absorber matrix to the fluid. This is a similar mechanism to that used in many convective heat exchangers, which incorporate tube bundles or pin fins.

Often the operating conditions demand that the absorber be physically separated from the ambient; e.g. when the flow is pressurized, or the working fluid is not air. In these cases the receiver must be equipped with a transparent window, which allows concentrated light to enter the receiver while separating the working gas from ambient air. Such pressurized volumetric receivers have been developed and tested in the WIS [67].

In a direct analogy with "conventional" catalytic applications [68,69] it becomes obvious that all three structured porous volumetric solar absorber modules shown in Fig. 7c can be coated with proper functional materials capable to perform/catalyse a variety of high-temperature chemical reactions – among them reforming – and thus be "transformed" and adapted to operate as solar chemical receiver/reactors where chemical reactions can take place in an efficient and elegant manner with the aid of the functional materials immobilized upon their porous walls [48]. Such devices comprise an integrated solar receiver – chemical reactor module, in which a catalyst-coated porous matrix volumetrically absorbs concentrated solar (radiant) energy directly at the catalyst sites, promoting heterogeneous reactions with gases flowing through the matrix (absorber) – thus they are frequently referred as directly irradiated volumetric receiver–reactors (acronym DIVRR). In this way absorbed radiation is converted from thermal to chemical form, thus storing solar energy in the chemical bonds of the reaction products rather than as thermal energy in a working fluid. On the other hand, direct heating in the case of receiver/reactors necessitates the use of a transparent window isolating the reactant gas streams from the ambient air and providing for reactor operation under non-atmospheric pressures if needed.

Each receiver/reactor type has its advantages and drawbacks; it is not therefore surprising that essentially all receiver/reactor concepts above have been used for solar-driven reforming to a higher or lower extent, having reached different scale-up levels. In fact, natural gas reforming has been the first process for solar conversion of hydrocarbons tested at an engineering scale of some hundreds of kilowatts of solar power input.

Additional issues have to do with the inherently transient nature of solar operation, requiring specific measures to prevent malfunctioning of the process and to avoid non-preferable process conditions. For instance, with respect to the carbon deposition issue mentioned above, during solar operation the dangerous region of temperatures where carbon deposition is likely to take place, is crossed at least twice a day upon morning start-up and

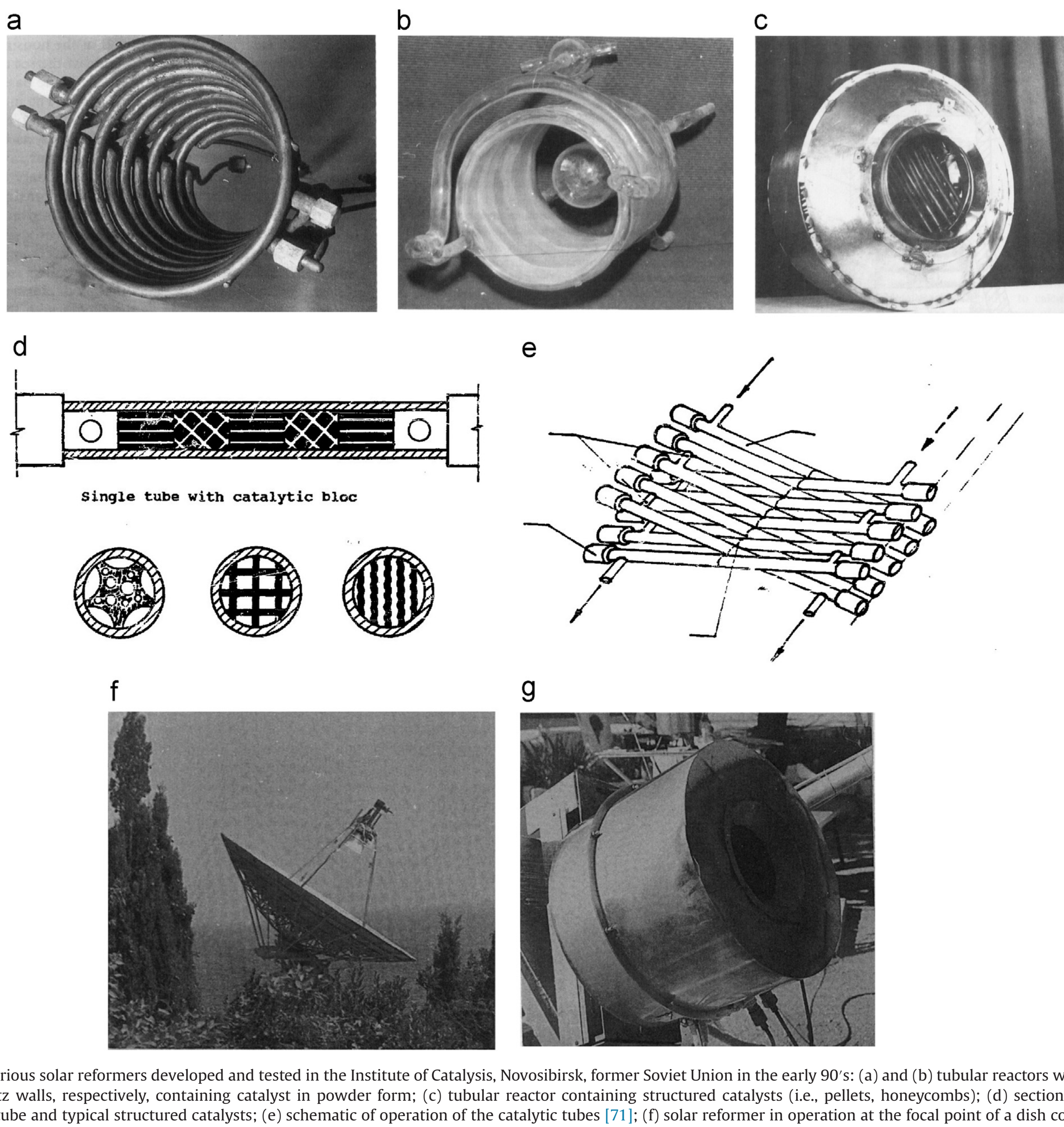


Fig. 9. Various solar reformers developed and tested in the Institute of Catalysis, Novosibirsk, former Soviet Union in the early 90′s: (a) and (b) tubular reactors with metallic and quartz walls, respectively, containing catalyst in powder form; (c) tubular reactor containing structured catalysts (i.e., pellets, honeycombs); (d) section of a single catalytic tube and typical structured catalysts; (e) schematic of operation of the catalytic tubes [71]; (f) solar reformer in operation at the focal point of a dish concentrator; (g) the solar reformer after operation [73].

daily shutdown. Therefore very specific and careful operational means has to be taken. The adjustment of mass flows and in particular the S/C ratio of the reactant gas will be an important parameter to control the process. A suitable process strategy can foresee for instance a switch-on of reactants′ flow after having reached a sufficient reaction temperature in the mornings and a switch off just after the Direct Normal Irradiance (DNI) has fallen below a certain threshold in the evenings.

3.3. *Worldwide research in solar thermal reforming of gaseous feedstocks*

3.3.1. *Solar thermal reforming of methane*

The concept of solar-driven reforming was first coined in 1982 by J. A. Chubb of the U.S. Naval Research Laboratory U.S.A., who proposed the CO_2/CH_4 reforming-methanation cycle as a mechanism for converting and transporting solar energy via solar receivers [52] and operated a solar tubular reformer with a Ruthenium (Ru) catalyst at the White Sands Solar Furnace [70]. Interest on this technology was revived at the late 1980s with the initial research in solar-driven reforming focusing on the concept of a closed loop for storage and transport of solar energy, in analogy to that with high temperature energy being supplied by a nuclear reactor. Parallel work took place during the same period at the Institute of Catalysis, Novosibirsk in the former Soviet Union [71–73] where Soviet researches designed and tested a variety of catalytic reforming reactors/receivers on the same research line of the CO_2/CH_4 reforming-methanation cycle mentioned above. Representative photographs of such tubular solar reformers containing either powder or structured catalysts tested during that time are shown in Fig. 9 [71]. In particular, solar steam reforming in a closed cycle has been demonstrated using a Ru reforming catalyst and a nickel methanation catalyst [73]. The solar catalytic reformer was positioned in the focal point of a parabolic dish (Fig. 9c). The reformer assembly contained in the insulated housing a water evaporator, a superheater of steam, a solar-flux receiving cavity around which the catalyst bed was located, and counter-current heat exchangers for recuperation of the heat of reaction products. Water evaporation and heating of steam to the temperature of the catalyst bed were accomplished solely at the expense of solar energy. The diameter of the reformer′s external housing was 42 cm, its height 34 cm and the weight of all reactors including the catalyst did not exceed 15 kg. The reaction was carried out at levels of total power input of incident solar energy ca 5 kW and pressures between 1.8 and 2.8 atm, where almost complete methane reforming was reported at gas temperatures at the catalyst bed outlet between 650 and 700 °C.

At the same time, the development of solar-based CO_2/CH_4 reforming technology was studied at the technical-scale in Israel and Germany as part of the International Energy Agency Solar Power and Chemical Energy Systems (SolarPACES) R&D program. Between 1988 and 1992, in an attempt to develop more economical, compact receivers for methane reforming, experiments on a laboratory scale were started at Sandia National Laboratories (SNL), U.S.A. [74], at DLR and at the WIS, both with indirectly heated tubular reactors as well as with the first windowed receiver–reactors where the catalyst was heated directly by a concentrated solar beam [75–77]. The technical characteristics and results of all these studies above were comparatively summarized [78].

A significant amount of work has been conducted over the last 25 years on the development and scale-up of the technology of solar reforming of methane and other hydrocarbons at DLR, WIS, and SNL, in several cases within joint Projects. Relevant research on solar reforming concepts is performed currently all over the world, principally by laboratories and research institutes that possess pilot-to-large scale CSP facilities such as the Plataforma Solar de Almeria, Spain operated by Centro De Investigaciones Energéticas, Medioambientales Y Tecnológicas (PSA-CIEMAT), the Eidgenoessische Technische Hochschule—Paul Scherrer Institute (ETH/PSI) in Zurich, Switzerland, the Ente per le Nuove tecnologie, l′ Energia e l′ Ambiente (ENEA) in Rome, Italy, in Europe, as well as by Department of Energy′s National Renewable Energy Laboratory (NREL), Sandia Corporation and the University of Colorado in U.S.A., the Commonwealth Scientific and Industrial Research Organization (CSIRO) in Newcastle, Australia, the Niigata University and the Tokyo Institute of Technology, in Japan and the Inha University in Korea, among others. The research activities can be divided into general reformer concepts and concepts for the improvement of the catalyst system (i.e., catalyst and structure that it is applied onto). Regarding the catalysts in solar reforming there are two major topics that require further development: the price for noble metal catalysts that are suitable for dry reforming of methane is too high for industrial application. Therefore, a Ni-based catalyst capable of performing dry reforming of methane without

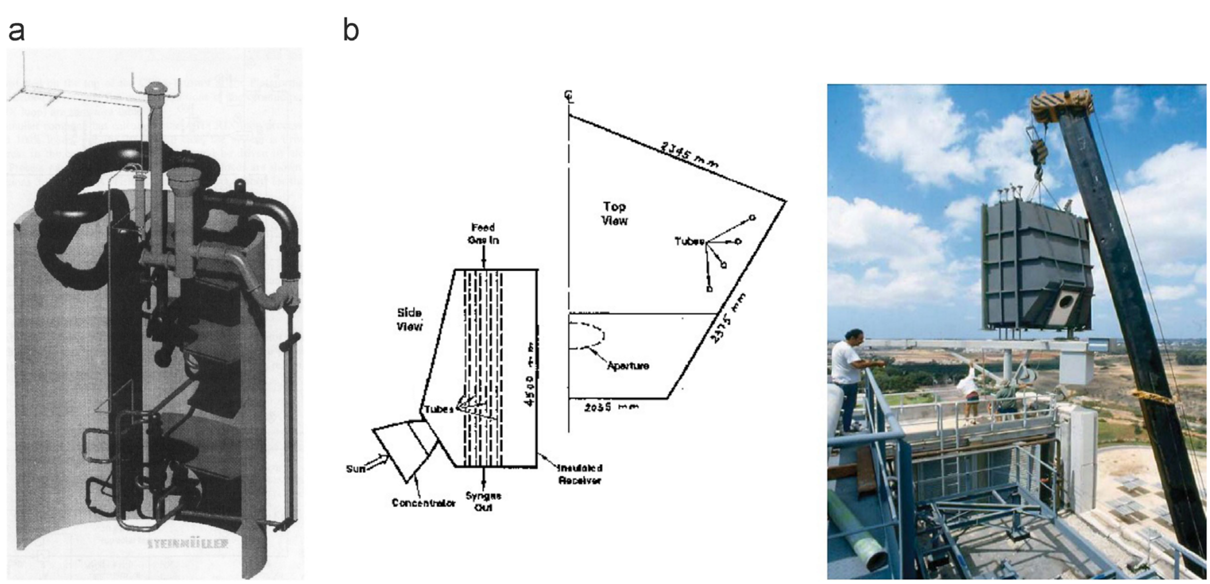


Fig. 10. Indirectly heated solar reformers using air as the heat transfer fluid: (a) ASTERIX reactor [82], (b) WIS′s; schematic (left) and installation of the reformer on the tower for solar operation (right) [42].

deactivation due to carbon deposition has to be developed [79]. The other obstacle exists in directly irradiated receiver/reactors. The catalytically activated absorber has to fulfill not only requirements regarding the chemical reaction but also the requirements regarding a solar absorber (i.e., high thermal shock resistance, low reflectivity and emissivity).

It is worth noting in passing that a considerable amount of work has also been conducted on methane cracking, or thermal decomposition to produce hydrogen and elemental carbon. This work will not be discussed in detail, although it should be recognized that the high temperatures required for this process (in excess of 1500 °C) make this technology less suitable for concentrated solar applications which appear best suited to processes below 1200 °C. It is further noted that due to this substantial energy penalty of the product hydrogen characterizing methane cracking in contrast to reforming, the economics of methane cracking are strongly dependent on achieving a reasonable price for the carbon by-product rendering the added value of the produced carbon black a key point. The selling price depends on the product′s nano-structure and applications in the fields of polymer composites and batteries are targeted [80]. Because of the unstable reaction conditions it is not proven yet that such a marketable carbon by-product will be available.

A detailed description of the various research efforts worldwide is presented below, grouped on the basis of the solar heating concept employed (indirect or direct) and sub-divided on the basis of the heat transfer medium employed in each case. In this context, the term “heat transfer medium” is used to define the medium that transfers the solar heat to the reactant gases (methane, steam, carbon dioxide). This classification has been adopted in order to delineate the technical characteristics of each approach rather than the chronological evolution of the technologies tested. The latter can be often confusing and circular since it depends from local factors; many technologies are tested in parallel all over the world, new concepts are first tested under lab- or simulated solar irradiation conditions whereas other, more mature concepts become implemented faster at pilot-scale solar plants through large bi- or multi-lateral research projects involving partners possessing large-scale solar facilities [81].

3.3.1.1. Indirectly heated reactors

Heat transfer medium: Air

This concept was first tested within the Advanced Steam Reforming of Methane in Heat Exchange (ASTERIX) project, a joint Spanish-German project carried out by CIEMAT and DLR in the late 1980s and early 1990s [82]. Within this experiment, the solar-driven Gas-Cooled Solar Tower (GAST) system at the Plataforma Solar de Almeria, Spain, was used to produce hot air (up to 0.36 kg/s at 1000 °C and 9 bar) to drive a separate steam reformer. This air is then fed back into the GAST cycle. In this case steam reforming of methane was performed in a 170 kW, tubular, 6-m long, packed catalyst bed reformer (Fig. 10a). A ceramic tubular receiver mounted on the central tower receiver at PSA was employed to generate this hot air. Both natural gas and demineralized water reactants were provided to the reforming packed catalyst bed unit pre-heated in preheaters coaxially installed in the reforming reactor and in a superheater to about 500 °C. Typically during the tests, solar-heated air was supplied to the reformer at 980 °C and exiting the reformer at approximately 420 °C, whereas the process gas mixture was heated through the catalyst bed from 500 to about 850 °C at the bed end. Final CH_4 conversions reported for air mass flows of 525 kg/h and water

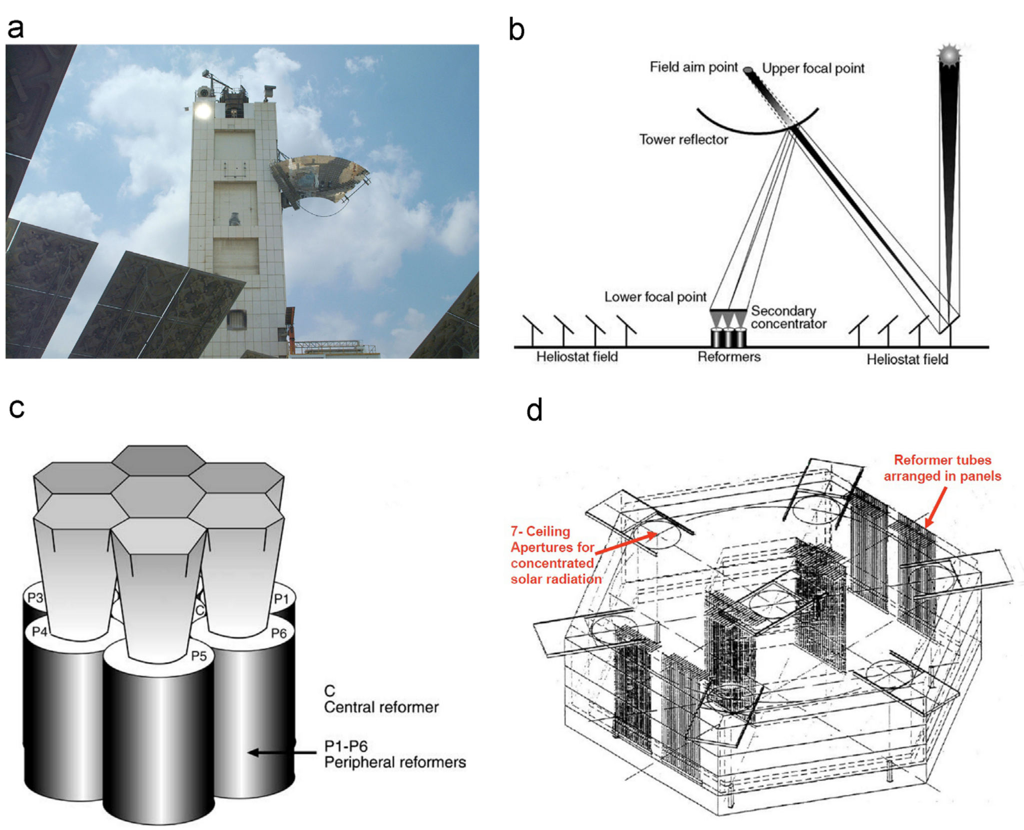


Fig. 11. WIS′s beam-down reformer technology: (a) beam down facility at WIS′s solar tower at Rehovot, Israel; (b) schematic of operating principle; (c) schematic of reformers′ cascade; (d) detailed schematic of construction on the ground [42,84].

mass flows from 26 to 39 kg/h were between 68 and 93% depending on the reformer's temperature that varied from 702 to 803 °C. The project demonstrated the technical feasibility of producing an industrial-quality synthesis gas under both steady state and transient solar conditions.

Solar reforming of methane by CO_2 in tubular reactors has also been studied at the WIS over the last two decades either as an open loop process for the production of syngas for power generation or as part of a closed loop reforming-methanation thermochemical heat pipe. Between 1993 and 1998 the WIS operated a solar central receiver for development of high-temperature technology, including the storage and transport of solar energy via CH_4 reforming [74]. The WIS facility was designed for testing reformers up to about 480 kW absorbed energy, for either steam or CO_2 reforming, operating between 1 and 18 bar. After laboratory-scale studies of the reactions in a solar furnace at

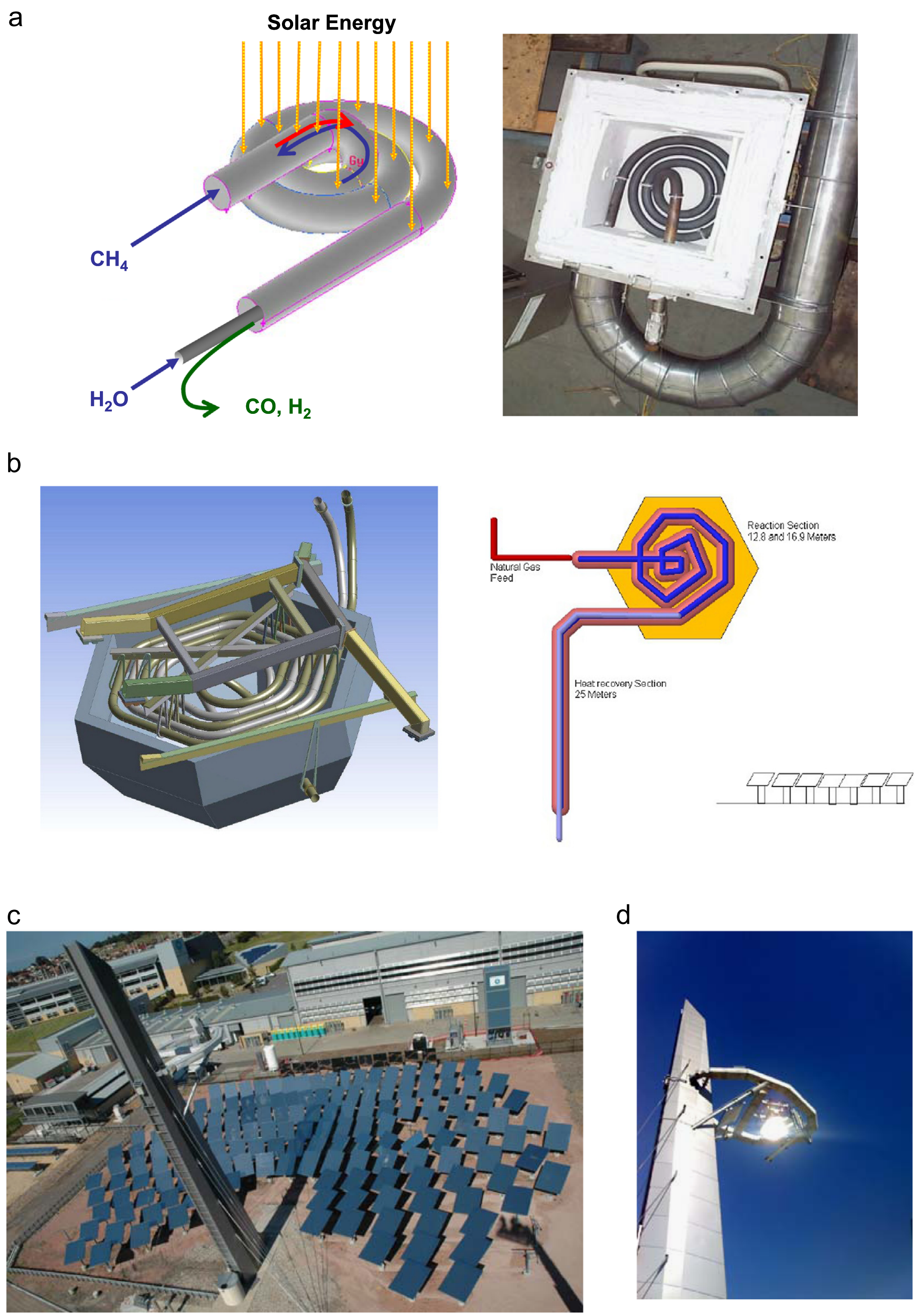


Fig. 12. CSIRO's reformer technology development: (a) the single coil solar reformer and its operating principle; (b) the double-coil reformer and its operating principle; (c) the single-tower, 500 kW, heliostat field at Newcastle site, Australia; (d) the reformer on the tower during solar operation [24].

the 5–10 kW scale, a 480 kW tubular reformer was constructed and tested under real solar conditions at the WIS central tower receiver. In contrast to the ASTERIX concept, in this case the reformer tubes were exposed to concentrated solar irradiation: a cavity receiver containing eight vertical 2.5-inch-diameter and 4.5-m-long reformer tubes was built, designed to produce syngas at 800 °C (Fig. 10b) [83].

However, because of its greater volume and weight, placing a tubular reformer on top of a solar tower was considered to be a major limiting factor to the large scale development of the tubular reformer concept. To address scalability issues WIS researchers transferred the concept to the so-called "beam down" receiver (Fig. 11 [84]); with the aid of an optical feature in the form of a 75 m^2 reflector shaped as a hyperboloid section attached to the tower at about 45 m above ground level (Fig. 11a), about one megawatt of concentrated sunlight can be reflected down onto a ground target. This optics allows a multi-megawatt tubular reformer to be built on the ground in a way resembling the construction of a conventional, commercial reformer with roof burners (Fig. 4a). The conceptual design of the ground tubular solar reformer comprised seven units—one central unit and six adjacent peripheral units, of a circular cross section with the tubular reactors having the proper geometrical dimensions in compliance with the power entering each reformer. Through an example, the performance of a complete, 50 MW_{th}, solar reforming system, including the entire optical path (heliostat field, tower reflector and secondary concentrators), heat transfer and kinetics of the reactions inside the reformer tubes has been modelled. However such a reformer has not been built and tested.

In Australia, the solar reforming of methane is particularly attractive in view of the country′s enormous areas of favourable insolation and its very large reserves of natural gas and coal bed methane that are co-located in many regions. Work in Australia on solar methane reforming has been conducted by CSIRO since the early 1990s aimed at catalyst and reactor development for conducting the CO_2-reforming reaction for application on both open- and closed-loop solar thermochemical heat pipes. CSIRO began work on solar reforming in 1999, with its 25 kW single coil reformer (SCORE); a schematic of its operating principle is shown in Fig. 12a. The catalyst is packed in-between the inner and outer tubes; the inner tube is purely for counter-current heating of the feed water stream. Production of solar-enriched fuels and hydrogen via steam reforming of natural gas (25 kW LHV) at temperatures and pressures up to 850 °C and 20 bar was demonstrated on this single-coiled reformer coupled to a 107 m^2 dish concentrator between 1998 and 2001. For the demonstration facility (2002), the reformer was designed for up to 1000 h of operation using a high temperature stainless steel whereas commercial nickel-based steam reforming catalyst was used to catalyse the reforming reactions.

Between 1998 and 2001 CSIRO successfully completed a $7.5 million project to demonstrate a solar thermal-fossil energy hybrid concept for solar-enriched fuels and electricity including solar steam reforming of natural gas to generate synthesis gas suitable for use as a fuel, further conversion of this gas to H_2 and CO_2 followed by recovery of CO_2 in a concentrated form and further purification of the gas by methanation to produce fuel cell-grade hydrogen (<10 ppm of CO). In 2004, CSIRO built a single-tower heliostat field of 500 kW capacity at its Newcastle site of National Solar Energy Centre (Fig. 12c) with the objective of demonstrating this solar reforming process on a larger scale. The reason for changing to a tower was the improved economics of the solar concentrator afforded by economies of scale. Solar resource at this site typically provided a direct normal incident radiation peak of $800-900$ W/m^2. In 2006 CSIRO demonstrated the solar steam reforming process operating on this solar tower over a commercial catalyst at reaction temperatures of $700-800$ °C and pressures of $5-10$ bar. Subsequently, CSIRO designed and installed in June 2009 a much larger, hexagonal-shape, dual-coil reformer (DCORE) capable of processing 200 kW thermal (LHV) natural gas at 10 bar and 850 °C (Fig. 12b and d). The length across the flats of the hexagonal shape coil is about 2 m making the outer receiver dimensions of about 2.5 m. Stable controlled reactor temperatures and consistent Hydrogen production were reported [85,86]. CSIRO has taken a different approach to most overseas investigators by focusing on developing and demonstrating solar-driven reformers that can achieve high methane conversions at lower temperatures (550–700 °C)) [87]. This has a number of significant advantages, including a reduction in heat losses due to radiation and convection so that the overall utilization of solar energy is maximized. In this respect CSIRO developed its own catalysts and claimed higher activity at lower operating temperatures – as low as 700 °C – compared to commercial reforming catalysts in three different reforming operation modes (low steam, mixed and CO_2 reforming).

Heat transfer medium: Sodium (Na) vapors

In this concept, liquid sodium contained in an evacuated chamber evaporates under the effect of concentrated sunlight impinging on one surface of the containment. The sodium vapor condenses on the reactor tubes in the chamber and liberates the heat of vaporization. Passive techniques (channels, wicks, gravity, etc.) return the liquid sodium to the absorber. Advantages claimed are the excellent heat transfer characteristics of evaporating and condensing sodium that result in uniform temperatures throughout the chamber ensuring therefore isothermal operation of the reactor tubes, with the rate of sodium condensation determined by the local energy requirements of the reaction. The proof-of-concept of such a reactor was first demonstrated for steam reforming under simulated solar conditions using infrared lamp heating ([57,88]) and subsequently under "real" solar irradiation within a SNL—WIS joint research project where a 20 kW sodium reflux solar reformer was built and tested at WIS′s solar furnace (1983–1984) for the CO_2 reforming of methane [89]. This receiver/reactor was a heat pipe with seven 2.5 m long tubes inside an evacuated metal box containing sodium. A schematic of the operation concept and actual reactor photographs are shown in Fig. 13. The catalyst was 0.5 wt% Rh supported on γ-alumina pellets 3.2 mm in diameter, filling two of the tubes in a packed bed configuration. The front surface of the box served as the solar absorber, consisting of a 3.2 mm Inconel plate, curved in one dimension to produce a more uniform solar flux distribution and to provide structural rigidity. In operation (Fig. 13e), concentrated sunlight heated the front plate and vaporized sodium from a wire mesh wick attached to the other side. In these experiments, the wall temperature of the reactors (taken as the temperature of the sodium vapor) was between 685 and 825 °C and the inlet flow rate (CH_4+CO_2) between 4400 and 6800 standard liters per hour (SLPH) under pressures 2–6 atm. The reactor′s temperature varied between 650 and 800 °C. Methane conversions between 50 and 70% were reported with an energy input between 1.5 and 7.8 kW. The experimental campaign was terminated prematurely due to an operational failure in the sodium evaporator, a fact that in combination with the flammability of Na vapors critically considered in the solar community caused the abandonment of this concept for some time. However, recently, sodium – and molten metal′s in general – as heat transfer fluids get back into the focus of a number of research groups with new results published [90].

Heat transfer medium: Molten salts

Molten salts, in particular some molten nitrates and carbonates

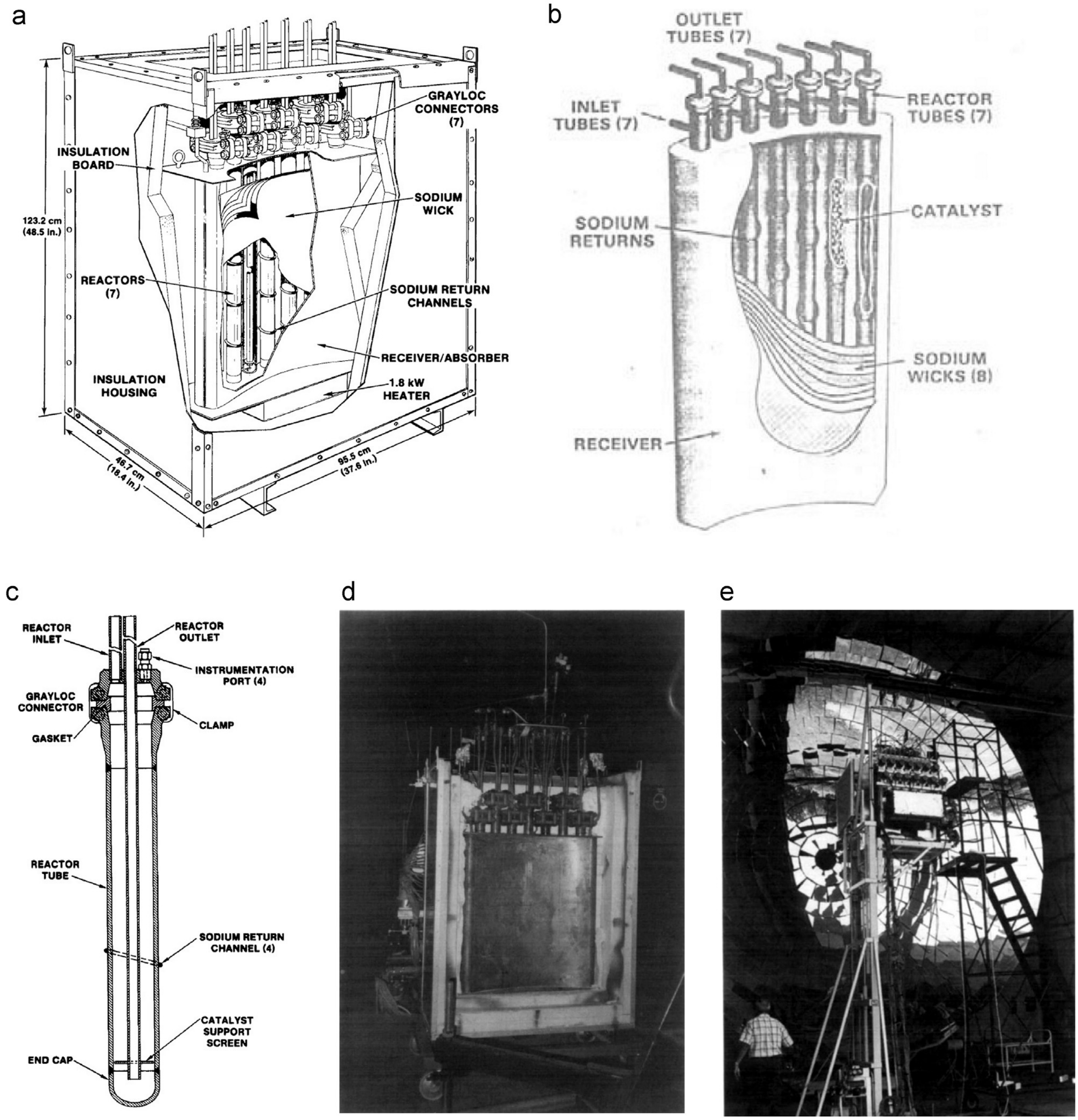


Fig. 13. SANDIA-WIS′s sodium reflux heat pipe solar receiver–reformer, built and tested at WIS′s solar furnace (1983–1984) for the CO_2 reforming of methane: (a) schematic drawing of the reactor; (b) heating concept principle; (c) details of a single reactor tube; (d) photograph of the receiver without the front panel; (e) the receiver installed in the facility at WIS′s solar tower [89].

mixtures, have been widely exploited as (sensible) heat storage materials in CSP plants, operating in the temperature range 300–600 °C. One of their disadvantages is that they decompose at temperatures higher than approximately 600 °C therefore up until recently they were used as large-scale solar heat storage materials only in parabolic trough CSP plants. However, molten salts such as $NaNO_3/KNO_3$ mixtures, have been employed in the recently inaugurated Gemasolar solar tower plant as combined heat transfer fluid/heat storage media operating at 565 °C [91]. Their attributes have lead several research groups to propose the utilization of thermal storage with a molten salt in order to provide constant-rate solar heat supply also for an energy demanding industrial chemical process like steam reforming.

The group of Niigata University, Japan, has proposed the concept of dry reforming of methane employing molten salts of the system K_2CO_3/Na_2CO_3 – that has an eutectic melting temperature of 710 °C – as the carrier material for the catalyst powder. In their initial configuration [92] the catalyst powder and the two salt components were mixed, and placed in a stainless steel cylindrical reactor (30 mm diameter and 300 mm length) heated via an infrared furnace at 950 °C. To enhance their contact with the catalyst, the preheated CH_4/CO_2 reactant gases were introduced through an aperture at the bottom of the reactor passing through the molten salt containing the catalyst powder. In this respect, according to the classification schemes above, this type of reactor can be classified as a “liquid bed” one—the authors

name it as a direct contact bubble reactor (DCBR) [93]. It is claimed that in this "bubbler" configuration the molten salt bath can in the one hand steadily supply solar heat inside the reactor under concentrated solar irradiation and in the other hand to avoid the loss of heat outside the reactor due to its high heat capacity. They tested in-house prepared non-noble-metal catalysts like Ni, Fe, Cu and W, supported on Al_2O_3, for activity and selectivity [94] as well as FeO aiming to produce H_2 from CH_4 via redox reactions [95] and concluded that among them Ni/Al_2O_3 was the most active and selective catalyst. They reported that under specific conditions about 70% of methane conversion was obtained in which the H_2/CO ratio in the product gas was approximately one. In subsequent studies [96,97] they replaced the "salt bath" with Ni-loaded porous alumina or zirconia spheres impregnated with the salt material (NaCl or Na_2CO_3) to improve upon heat storage/release characteristics. Currently in cooperation with Inha University, Korea [98] this concept has culminated to a double walled tubular receiver–reactor called MoSTAR (Molten-Salt Tubular Absorber/Reformer) where the inner tube is filled with catalyst balls and the space between the inner tube and the outer absorber tube is filled with the composition of a phase change material (carbonate) and a ceramic material (MgO) to increase the composition′s thermal conductivity. Two different sized reactor tubes were constructed and tested for dry reforming of methane during cooling or heat-discharge mode of the reactor tube using an electric furnace successfully sustaining methane conversion above 90% under feed gas mixture of $CH_4/CO_2 = 1{:}3$ at a residence time of 0.36 s, 1 atm and reaction temperature of 920 °C. This concept aims to allow steady state conditions in the reactor tube even during cloud passages. The next step of the project is to demonstrate the performance of such "double-walled" tubular absorbers/reformers with molten-salt thermal storage reactors on-sun with a 5-kW$_t$ dish-type solar concentrator.

Instead of employing the molten salt inside the reformer reactor, the group at ENEA, Italy has put forward the idea to heat a tubular reformer externally ("allothermally") by a molten salt, more or less in the same way that the industrial classical reformers are heated by hot combustion gases, or, in other words, employing the ASTERIX concept described above for decoupling the solar receiver from the reformer but using molten salts instead of air for heating the latter. Materialization of this concept would enable coupling of allothermal reformers to parabolic trough solar plants; however this also implies that the particular reaction has to be performed at temperatures lower than 565 °C. As already mentioned, one of the ideas in this direction is to employ membrane reactors where the selective removal of hydrogen from the products′ stream enhances the conversion and allows for performing the reaction at lower temperatures [99]. ENEA is working on this direction; they have first provided an analysis of such a plant including a parabolic trough, a two-tank molten salt storage system and either a single tubular steam methane reforming (SMR) reactor with partial recirculation of the product mixture after hydrogen removal in a downstream permeator or a cascade of such SMR reactors [100]. SMR reactors have been modeled as 12-m-long, double tube heat exchangers, with gas mixture entering the inner tube packed with catalyst bed at 500 °C, and molten salts counter-current flowing in the annular zone entering at 550 °C and with about 530 °C exit temperature. All chemical process configurations have been analyzed at nominal pressures of 10 and 20 bar, and 2.2 mol/mol steam-to-carbon ratio into the first SMR

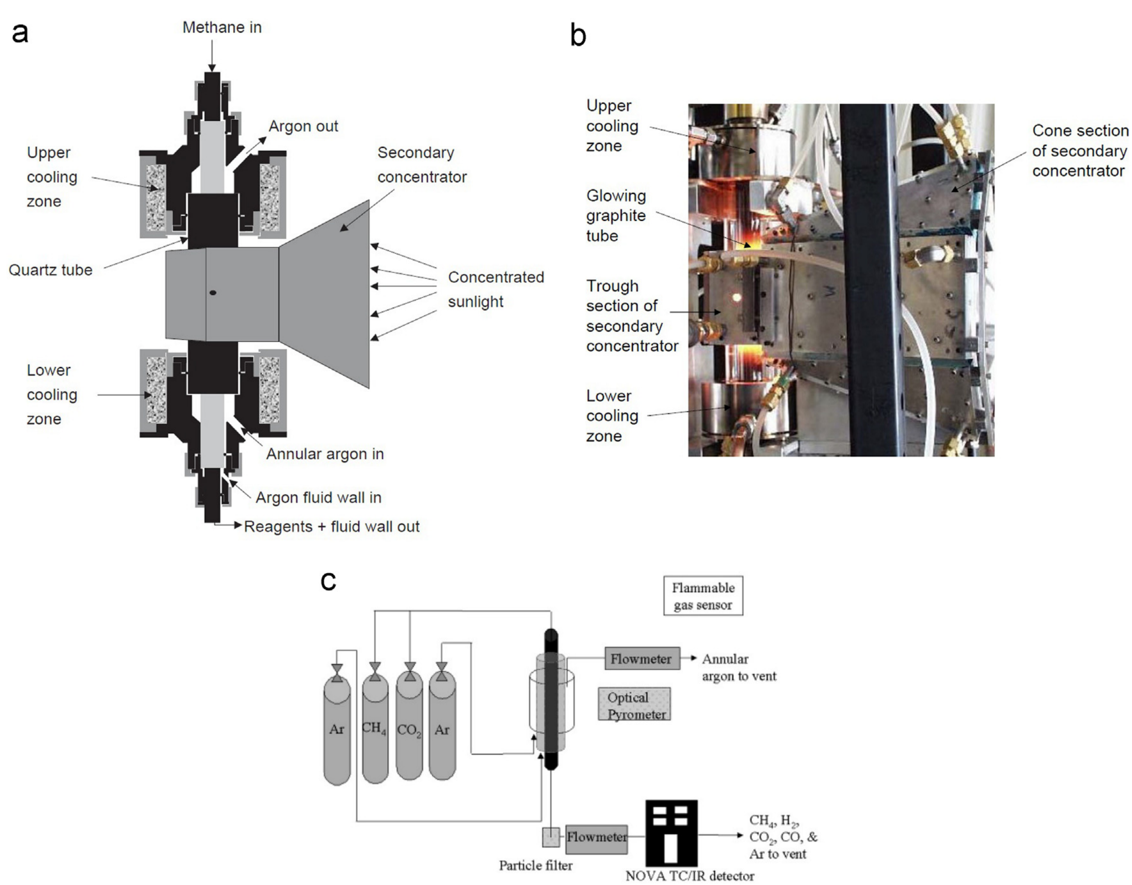


Fig. 14. University of Colorado′s solar-thermal aerosol reactor: (a) schematic and (b) photograph of actual reactor heated to approximately 1200 °C, showing secondary concentrator, cooling zones, quartz tube and solid graphite tube; (c) schematic of operating process [15].

reactor. As far as the membrane modules are concerned, the use of Pd-based thin layer membranes supported on a ceramic or metallic material operating at 500 °C was assumed; moreover, membranes were supposedly sized so as to remove 85% of the inlet hydrogen with 100% selectivity. In subsequent studies [101] they adopted a heat-exchanger-shaped (shell-and-tube) reactor, optimized its dimensions and assessed its performance concluding that a reactor 3.5 m long and with a diameter of 2 in. is the most efficient in terms of methane conversion (14.8%) and catalyst efficiency. However, due to the small methane conversion, this concept does not yield syngas but enriched methane (EM), i.e. methane with 17% % Hydrogen. Engineering and experimental activities aimed to the development of a prototype apparatus are now in progress in ENEA's laboratories.

Heat transfer medium: Solid particles

A somewhat different approach to solar-driven CO_2-reforming is being investigated at NREL and the Department of Chemical Engineering at the University of Colorado, U.S.A. In this approach what is heated by concentrated solar radiation is a "target" graphite tube than can thus reach ultra-high temperatures (around 1900 °C) under non-oxidative atmosphere. The same reactor configuration principle can be used for either the solar thermal dissociation of methane to hydrogen and carbon black or for non-catalytic CO_2 methane reforming to produce syngas [102]. For the latter case, a triple-tube, solar powered, fluid-wall aerosol flow reactor design has been used in the High Flux Solar Furnace (HFSF) facility at the NREL to produce syngas with a lower H_2/CO ratio, as required for Fischer–Tropsch synthesis [103]. The furnace delivered a concentrated sunlight beam approximately 0.1 m in diameter to the reactor, reflected via a secondary concentrator. A schematic and a photograph of the reactor are shown in Fig. 14a [15]. The reactor was composed of three concentric vertical tubes: an innermost tube made of porous graphite, a central tube made of solid graphite, and an outer tube made of quartz. The sunlight through the quartz tube heated the center solid graphite tube, which then radiated to the porous graphite tube. Argon was fed into the annular region between the two graphite tubes and the gas was forced through the porous tube wall. It served to protect the inner tube wall from carbon particle deposition. In this case, carbon particles are produced in-situ as a by-product: it is though claimed that these are not detrimental to the process but on the contrary, are preferably flowed with reactant gas through the reactor tube as radiation absorbers to facilitate heating and reaction—justifying the terminology of "aerosol" reactor. The methane and carbon dioxide were fed into the top of the porous graphite tube, and the reaction products as well as the fluid-wall gas exited the bottom of the reactor. Operating with residence times of the order of 10 ms and temperatures of approximately 1700 °C, methane and CO_2 conversions of 70% and 65%, respectively, were obtained in the absence of any added catalysts. CH_4/CO_2 ratios of 1, 1.5 and 2 were used and it was found that ratios greater than 1 were needed with this system to prevent CO_2 attacking the graphite wall of the reactor.

3.3.1.2. Directly irradiated reactors

Structured reactors based on ceramic honeycombs

Researchers at WIS have deposited Rh on an alumina honeycomb and irradiated it in their solar furnace through a sapphire window to catalyze the reaction of CO_2 methane reforming [77]. Due to failure issues the sapphire window was later substituted by a fused silica bell jar reactor that was tested in the same facility in the configuration shown in Fig. 15 [76]. The catalysts were two samples (12 and 25 cm thick) of cordierite honeycomb with 4 mm square holes and 0.5 mm wall thickness, first coated with a high surface area alumina washcoat, followed by deposition of Rh. When a temperature of about 800 °C was reached on the surface of the catalyst, methane was added, keeping the ratio of CO_2/CH_4 at about 1.3. Reported methane conversions reached 67%. However methane reformers based on honeycombs have not been reported of being scaled-up.

Structured reactors based on ceramic foams

In fact such reactors based on ceramic foams were the first structured reactors to be tested for solar-aided methane reforming and today are the most developed ones tested on a level of a few hundred kilowatts of solar input. Their prevalence over honeycomb reactors for the particular high-pressure application should be sought to their inherently higher porosity that allows for solar radiation to penetrate deeper in the volume of the materials [104] as well as to their sufficient radial heat transfer mechanism that prevents flow instabilities at the high temperatures encountered during solar operation [62]. The first examples of such solar reactors can be traced back in 1990 when solar reforming of methane with CO_2 in a directly irradiated volumetric receiver–reactor was first demonstrated in the "CAtalytically Enhanced Solar Absorption Receiver" (CAESAR) experiment conducted by SNL, Albuquerque, NM, U.S.A. and DLR, Germany [105] between 1987 and 90. Reticulated porous α-alumina-mullite foam disks, coated with a γ-alumina washcoat and loaded with Rh catalyst, were assembled in a multi-layered flat-disk configuration (Fig. 16a) within an absorber (Fig. 16c), located behind a quartz window aperture and directly irradiated by concentrated solar energy (Fig. 16b). Reactants flowed through the disk and products removed from the back of the receiver, placed in the focal point of a parabolic dish capable of 1–50 kW solar power (Fig. 16d). The total solar power absorbed reached values up to 97 kW and the maximum methane conversion was almost 70%. Receiver efficiencies ranged up to 85% and chemical efficiencies peaked at 54% demonstrating the "proof-of-concept" of carbon dioxide reforming of methane in a 100 kW receiver–reactor mounted on a large solar thermal concentrating dish. In this project, the process control

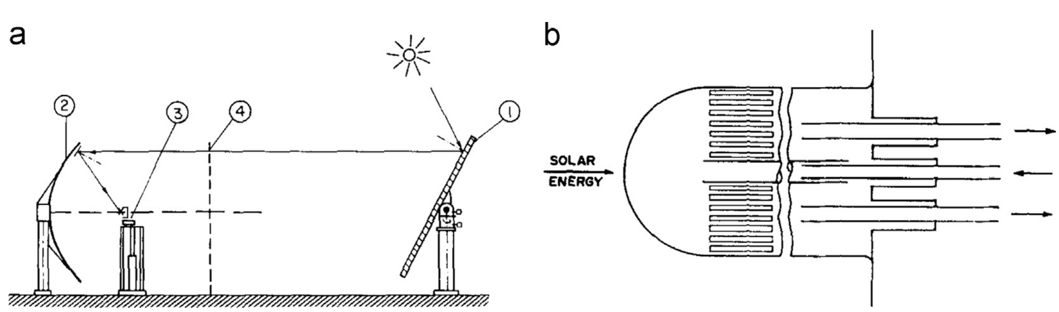


Fig. 15. WIS's honeycomb solar reforming reactor: (a) diagram of the Schaeffer Solar Furnace test facility: (1) flat heliostat; (2) spherical concentrator; (3) hydraulic table with the experimental set-up; (4) furnace doors; (b) sketch of WIZ's transparent bell jar solar reactor with the honeycomb catalyst [76].

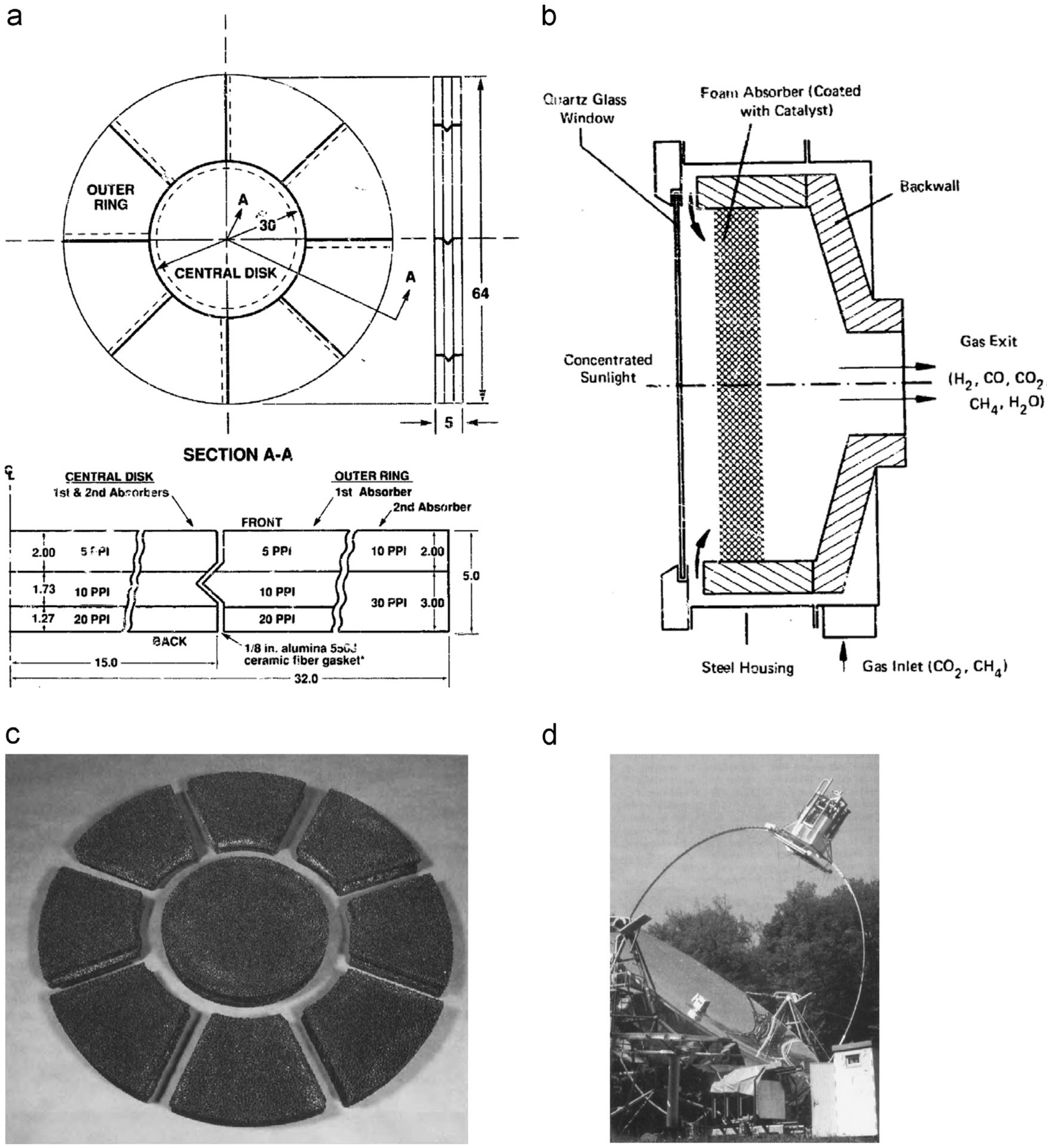


Fig. 16. (a) Sketch of CEASAR multi-layer foam absorber′s structure; (b) schematic of receiver/reactor′s operation; (c) actual photograph of first CEASAR receiver; (d) actual reactor on parabolic dish test facility [105].

strategy of varying the flow of reactants to the receiver to cope with the unsteady solar energy input was demonstrated to be technically feasible in a 100 kW receiver/reactor mounted on a large solar thermal concentrating dish.

A second generation solar chemical receiver–reactor was designed for a power input of up to 300 kW, and built in 1993–1994 for operation as part of a closed thermochemical storage and transportation loop within a joint project between the Weizmann Institute of Science (WIS) in Israel and DLR [50,106]. The main reactor improvements with respect to the CAESAR one were the installation of a higher power unit and a parabolic quartz window behind of which the receiver foam pieces were arranged in a domed cavity configuration (Fig. 17b). For solar testing, the assembled receiver was installed on top of the tower of the WIS Solar Test Facility Unit in Rehovot, Israel. Because of their low thermal shock resistance, Al_2O_3 foams were eventually substituted by SiC ones (10PPI, 94% porosity, surface area of 550 m^2/m^3) and then coated with 10% of γ-Al_2O_3 washcoat and 11 wt% of Rh (with respect to mass of the washcoat). The power absorbed by the reactor was between 200 and 300 kW. Despite local degradation effects, the absorbers performed well during solar operation. Typical operating temperatures ranged from 700 °C to 860 °C, with an absolute pressure of 3.5 bar, reaching methane conversions of 84–88%. The receiver is currently on display at DLRs facilities in Cologne, Germany (Fig. 17c and d).

These ceramic-foam-based solar reactors were pursued further within Project SOLASYS (partners: DLR, WIS and Ormat Pty Ltd, an Israeli company with expertise in gas turbines and related technologies), where the technical feasibility of solar reforming with Liquid Petroleum Gas (LPG) as feedstock and combustion of the product gases (syngas mixture) in a gas turbine to generate electricity at the 300 kW_e-scale was successfully demonstrated. During the test period on WIS solar tower (Fig. 17c and d) the solar reformer was operated in the power range 100–220 kW producing syngas at 8.5 bar and 760 °C with conversion rates close to chemical equilibrium.

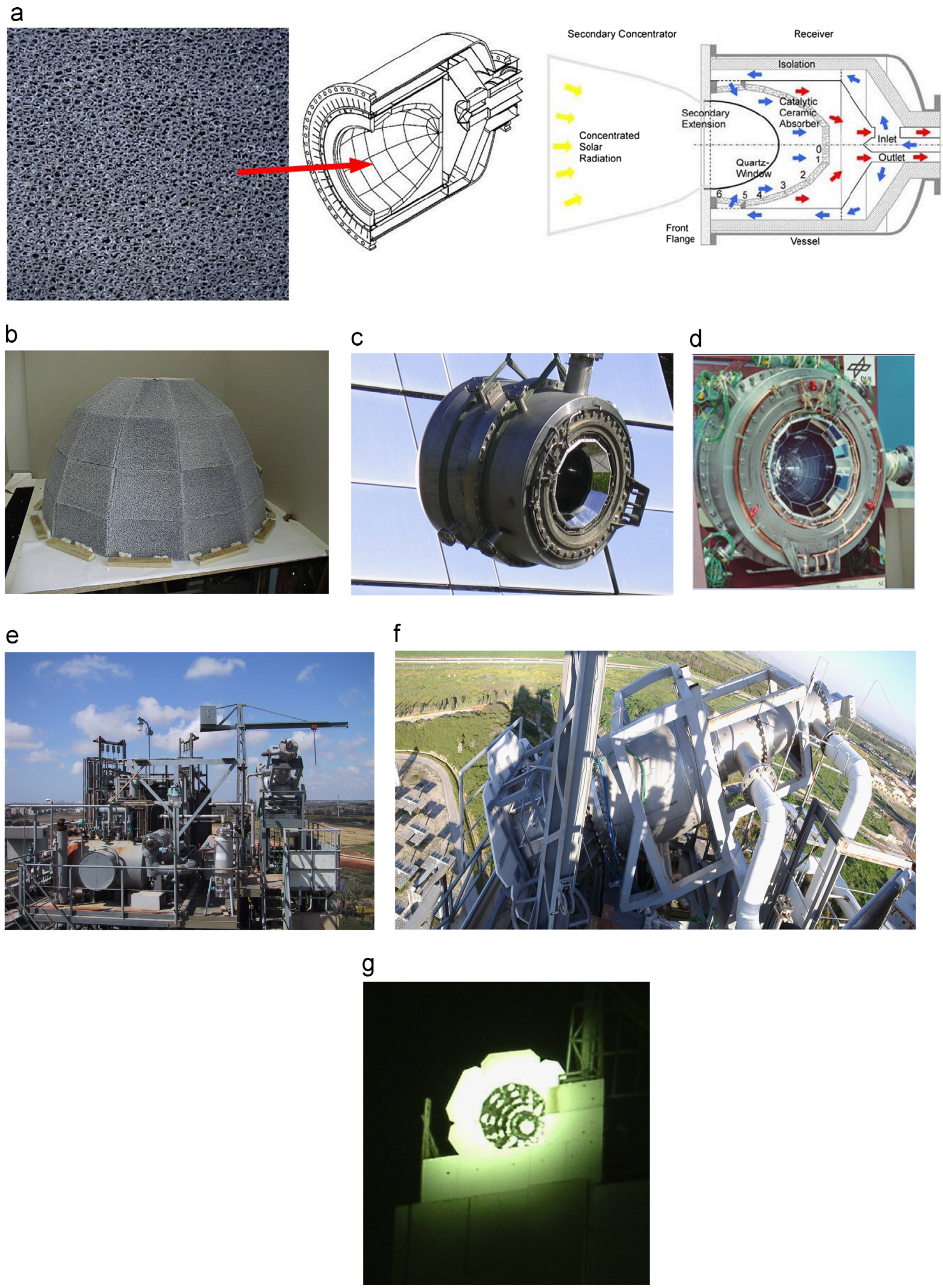


Fig. 17. The SOLASYS ceramic foam-based directly irradiated (DIVVRR) solar steam methane reformer: (a) sketch and operating principle; (b) assembled dome of the solar receiver (c) and (d) actual reactor photographs; (e) reactor installation on top of the solar tower of the WIS, Israel; (f) close-up photograph of the reformer installed on top of the tower; (g) reformer in operation [24].

An advanced and more compact and cost-effective volumetric receiver/reformer has been developed within the successor Project SOLREF with the rationale to operate at a higher power level (400 kW_e) as well as at higher pressure and temperature conditions, e.g. 950 °C and 15 bar, which would result in higher conversion rate of methane to hydrogen and higher efficiency (Fig. 18a).

Among the innovative modifications implemented was a new catalytic system capable of operating at higher temperatures allowing thus a broad range of feed compositions – biogas, landfill gas and contaminated natural gas (CH_4 with a high content of CO_2) – to be processed and avoiding carbon deposition in the reformer reactor. An advanced solar reformer was developed, tested and validated under real solar conditions at the WIS (Fig. 18b). A test campaign was carried out demonstrating the feasibility of the SOLREF technology. Relevant publications claim that the cost for hydrogen produced by solar steam reforming of methane is very close to conventional steam reforming with the break-even point being at a natural gas price of 0.35 €/m^3 [13,107].

The same Japanese group from Niigata University mentioned above, has also studied CO_2-reforming on laboratory scale using a new type of catalytically-activated "metallic foam" absorber, directly irradiated by a solar-simulated Xenon lamp light and subjected to solar flux levels in the range 180–250 kW/m^2 [108]. The absorber consisted of a Ni–Cr–Al alloy, containing Ru/Al_2O_3 as the catalyst and was found to have a superior thermal performance in terms of absorbing solar energy and converting it into chemical energy via the reforming reaction, at relatively low solar fluxes when compared to the conventional ceramic foam absorbers. In a later study on the same system [109] they examined the kinetics of this reaction in the temperature range 650–900 °C and analyzed the kinetic data by four different types of kinetic models vs. experimental reforming rates. In a series of parallel publications [110,111], the same group tested in the same Xe-lamp rig a series of Ni-based catalysts in combination with Ru and supported on magnesia- and alumina-based carriers (Ni–Mg–O, Ni/Al_2O_3, Ru/Al_2O_3 and Ru/Ni–Mg–O) trying to establish robust catalytic systems free of expensive metals like Ru or Rh, first in powder form and subsequently coated on Al_2O_3 and SiC foams reporting for the latter methane conversion reaching 80% at a reforming temperature of 950 °C. The current status of this development is

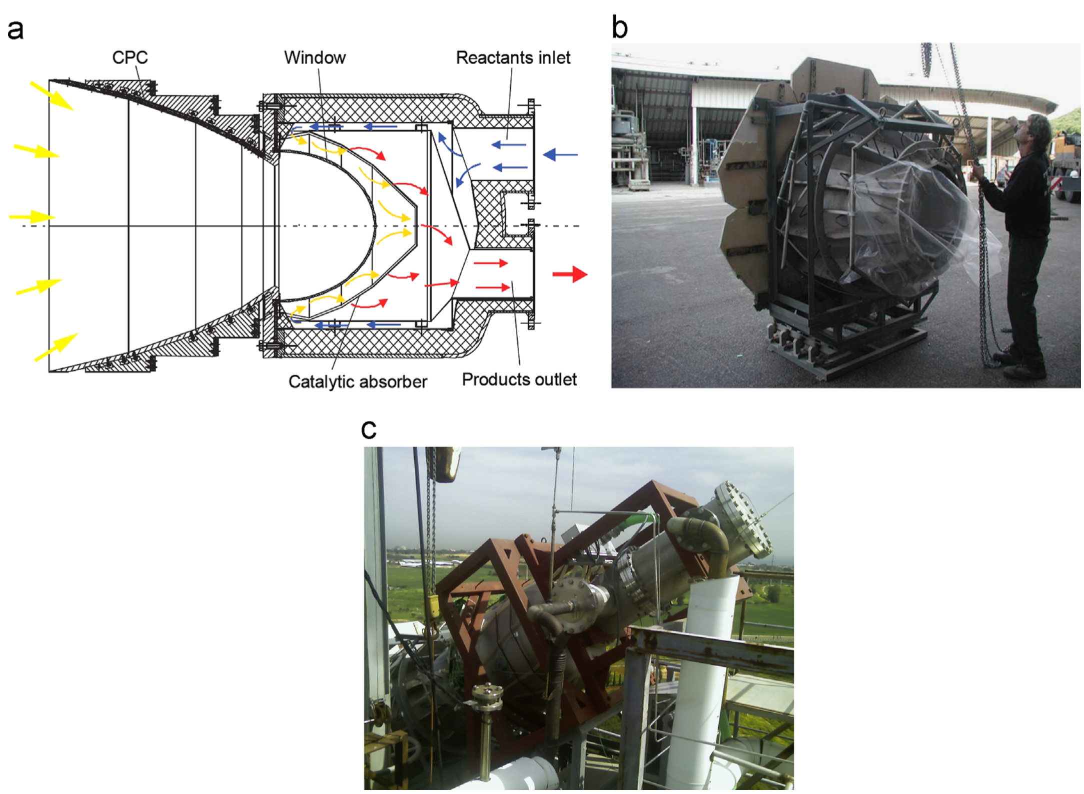


Fig. 18. The SOLREF DIVVRR: (a) sketch of operation principle; (b) assembled solar steam reformer reactor ready for transportation; (c) actual reactor installed on top of the solar tower of the WIS, Israel [42].

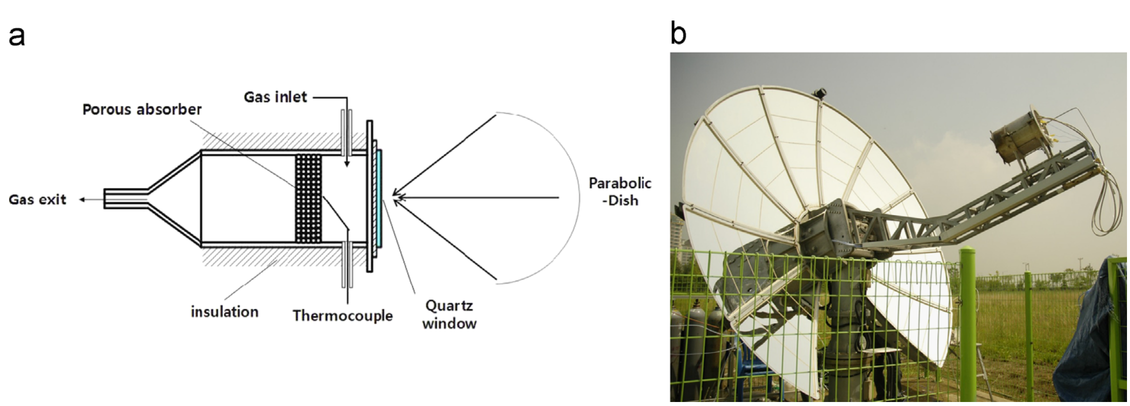


Fig. 19. The metallic-foam-based reactor of Inha University, Korea: (a) sketch of operation principle; (b) the 5-kW$_{th}$ absorber/reactor used for CO_2 reforming of methane on the Solar Dish System (INHA-DISH1) [81].

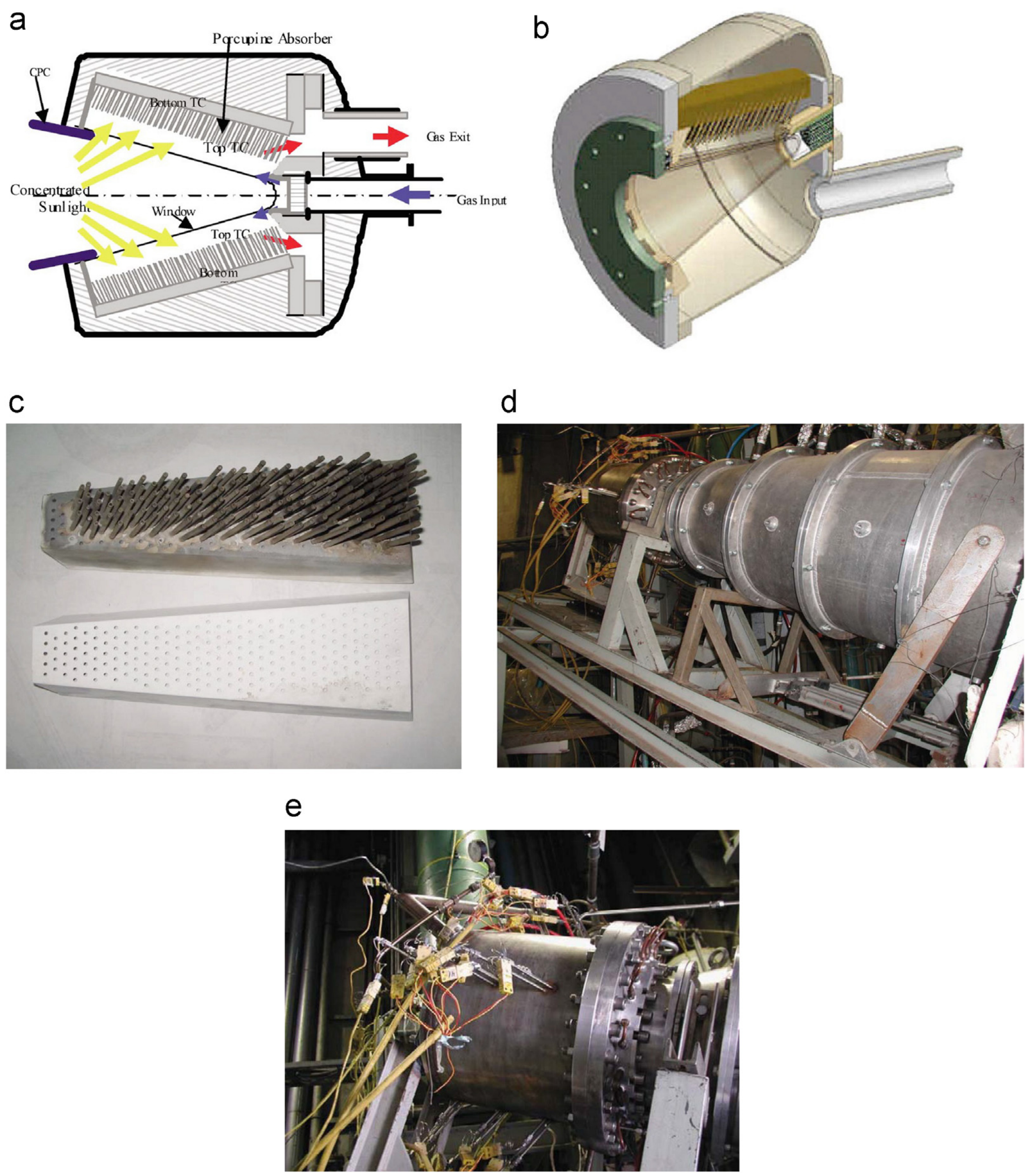


Fig. 20. WIZ's "Porcupine" directly irradiated solar reformer: (a) schematic of the reformer design and operating principle; (b) 3-D representation of reactor's geometry; (c) actual absorber sections made of alumina base, before (bottom) and after (top) inserting alumina.

that the system of choice for subsequent scale-up is a Ni/MgO–Al_2O_3 catalyst coated on SiC foams [111].

Researchers from Inha University in Korea are also investigating structured reactors based on metallic foams for CO_2 methane reforming. They have proposed and developed a double-layer metal foam absorber/reactor in which the front part is not catalytically active but realizes the absorbing of solar radiation and heat transfer to the gaseous reactants fluid. The rear part is a Ni metal foam coated with Ni/Al_2O_3 catalyst. The absorber was tested in several campaigns with respect to solar CO_2 reforming of methane on a parabolic dish capable of providing 5-kW_{th} solar power (INHA DISH1—Fig. 19 [81]). The temperature at the center of the irradiated surface of the absorber ranged from 900 to 1000 °C, the total power input of the incident solar energy into the absorbers was 3.25 kW at steady-state operating conditions, and the maximum CH_4 conversion reached 60% [112]. Compared to "conventional" catalytically activated ceramic foam absorbers, direct irradiation of the metallic foam absorber was claimed to exhibit superior reaction performance at relatively low insolation or at low temperatures and better thermal resistance preventing cracking by mechanical stress or thermal shock. In addition, the double layer absorber helped to maintain higher temperature profiles in the reactor during the heating mode that alleviated deactivation of catalytically-activated metal foam and, consequently, sustained high methane conversion for much longer during the heating and cooling mode of the reactor.

Structured reactors based on fins

WIS's researchers have designed a reformer based on the directly irradiated annular pressurized receiver (DIAPR) [67] and the "porcupine" concept, for operation at high temperatures and pressures. A schematic of the reformer design and operating principle is shown in Fig. 20a [113] and a 3-D representation of its geometry in Fig. 20b [114]. Catalytic elements for use in this reformer based on Ru/Al_2O_3 promoted with Mn oxides to avoid carbon deposition were developed, characterized and supported on alumina pins by washcoating; long-term tested confirmed their chemical and thermal stability even after calcinations at 1100 °C for 500 h under argon flow [113,115]. With input from computational models that identified initial design inefficiencies [114] and corrective actions taken therein, a prototype "porcupine" reformer using a conical quartz window was built

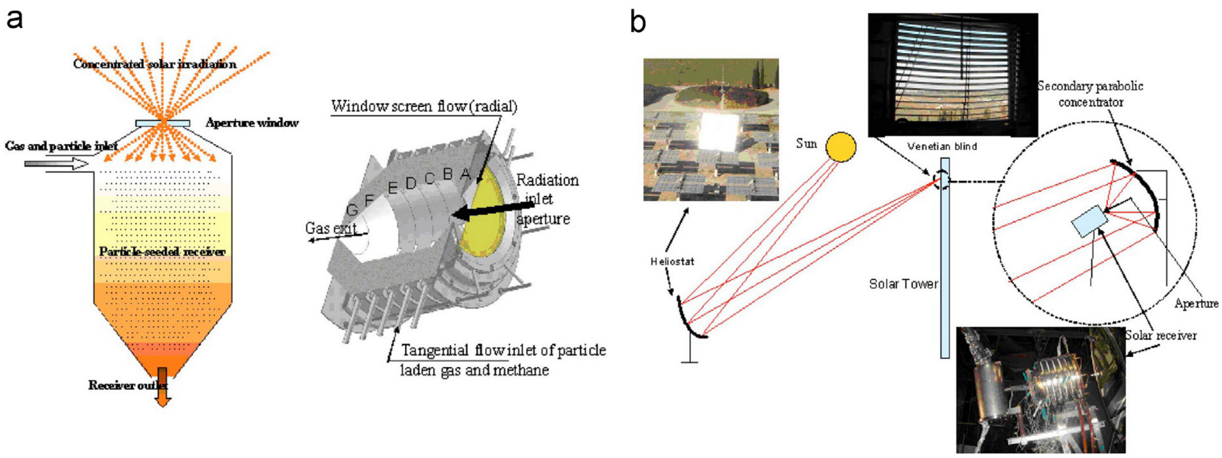


Fig. 21. WIZ′s directly irradiated particle solar receiver: a schematic of the operation principle of such a receiver and of the solar receiver actually used in the experiments; (b) optical system for the solar experiments [117].

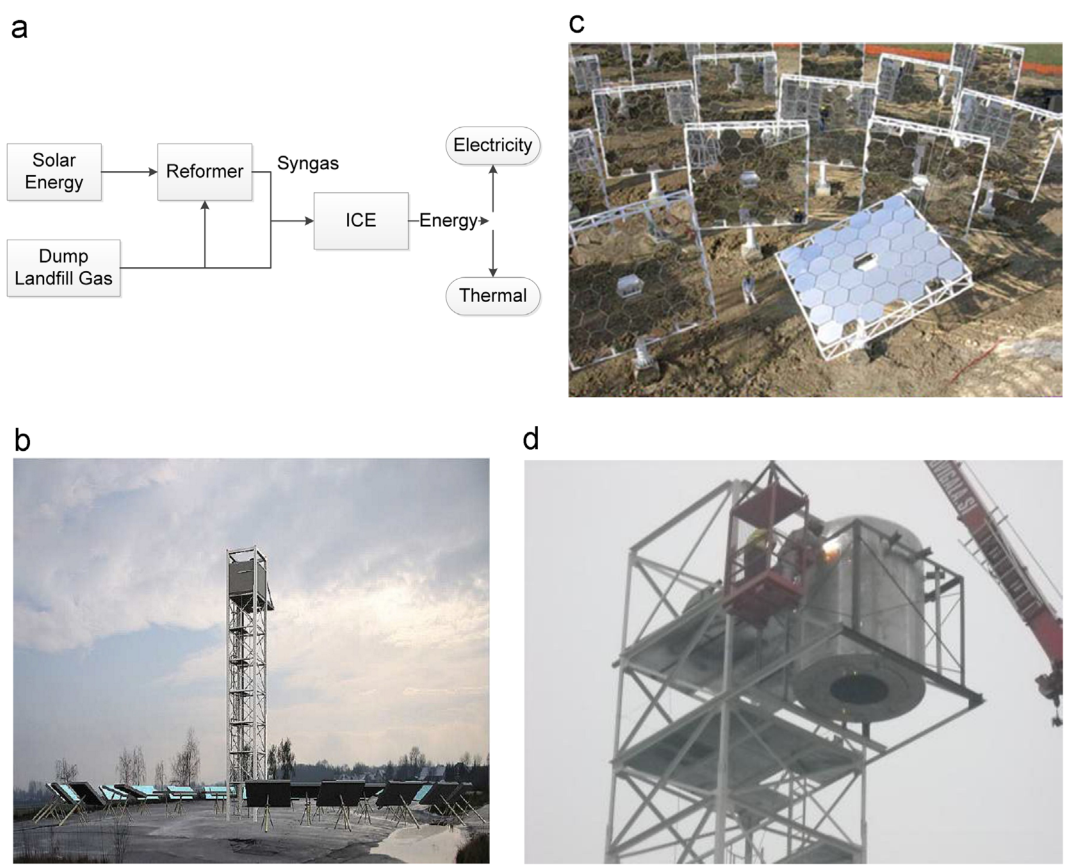


Fig. 22. The SOLBIOPOLYSY technology for solar-aided reforming of landfill gas: (a) schematic of the polygeneration concept implemented; (b) the solar platform built in Ptuj, Slovenia; (c) heliostat details; (d) the reformer placed on top of the solar tower [118].

(Fig. 20b–e) [42,116] and tested with respect to CO_2 methane reforming on the solar tower of WIS in 2010. The CO_2 to CH_4 ratio was about 1:1.2. Eight test runs were performed, focusing on the influence of gas pressure and flow rate on the CH_4 conversion. Gas pressure was varied between 4 and 9 atm and the total inlet flow rate between 100 and 235 standard liters per minute. The maximum absorber temperature was kept below 1200 °C. The conversion of CH_4 reached 85%. The results indicated that this type of volumetric reactor can be used effectively for CO_2 reforming of CH_4; further work aimed at improving the total efficiency of the system is in progress.

Non-structured reactors based on solid particles

Researchers at WIS performed dry methane reforming with carbon dioxide in a directly irradiated particle receiver seeded with carbon black particles in a molar ratio of C/CO_2 about 0.5/100 and with CO_2/CH_4 inlet ratios varying from 1:1 to 1:6 [117]. The receiver uses a moving radiation absorber, i.e. particles entrained in the reforming gas mixture that have two functions: to absorb the solar radiation and transfer it to the gas and to act as a reaction surface for the reforming reactions (Fig. 21). Dry solar reforming was conducted without any catalyst at a temperature between 950 °C and 1450 °C at the WIS′s solar tower, using primary and secondary

concentrators to reach a solar flux of up to 3 MW/m^2 at the receiver aperture. The exit gas temperatures were 1100–1450 °C. Depending on the temperature, a share of the carbon particles reacted with CO_2 to form CO, i.e. the particles in the receiver were gradually partially or totally consumed. The reforming experiments indicated that the carbon black particles entrained in the gas flow augmented the reaction of methane cracking.

3.3.2. Solar thermal reforming of biogas

The only example of solar-aided reforming of gaseous feedstocks other than methane reported so far is within the context of the EU-funded project "SOLBIOPOLYSY—Biofuel Polygeneration System integrating MSW Landfill Gas and Solar Energy" that took place between 2008 and 2011 with partners from Italy, Slovenia, Greece and Portugal [118] The over-all concept was first to reform in-situ the biogas to syngas and further combust a mixture of biogas and syngas in an internal combustion engine for electricity generation (Fig. 22a). In this perspective, a 250 kW pilot plant was constructed near Ptuj, Slovenia, in an old, non-active landfill site, consisting of all the necessary infrastructure (Fig. 22b)—an ICE engine, a heliostat field, a 25-m high solar tower, landfill gas installation, heat exchangers, etc. A solar reformer for the processing of landfill gas was developed and in-situ tested on the top of the solar tower (Fig. 22c). Steam reforming was reportedly performed at temperatures higher than 700 °C and pressures 0.5–10 atm.

4. Current development status and future prospects

While the long-term incentives for solar thermochemistry may be apparent, there is a need to search for near-term applications to establish priorities for R&D activities and to attract support from funding agencies and industry. In this perspective, for the subsequent scale-up of current solar methane reforming technologies to demonstration level, several choices have to be made with respect to certain issues that will impact the ability of the technology to enter the marketplace.

With respect to the CSP technology to be employed, as already mentioned, coupling of the reforming reaction to the currently most commercially developed parabolic trough CSP plants [8,119,120] via molten-salts allothermal heating still has inherent problems with the low temperature levels that can be reached. Solar dish collectors focus the solar energy (typically 10—400 kW_{th}) to a receiver mounted at the focus of the dish. Even though the first solar-coupling step of many of the reforming studies above has been the testing of reactors positioned at the focal point of a solar dish receiver, the fact that the receiver/reactor thus has to move with the dish as the latter tracks the sun complicates the scale-up of the technology. On the other hand, solar dish collectors are inherently modular: in order to generate large amount of steam and power via parabolic dish, many receivers and similar number of parabolic dishes are needed to hold them, pressurized water has to be pumped to each dish and the steam to be collected to a central power block [121]. Thus, even though higher conversion efficiency from solar to electricity in each individual dish is an advantage over solar tower and solar trough systems, the dish is likely to be a viable solution more for pilot scale experiments and distributed applications like destruction of toxic wastes. Very recently, though, an approach towards developing a solar thermochemical reaction system based upon the integration of parabolic dish concentrators and process-intensive, micro- and meso-channel process technology, with an advanced combined-cycle power system was presented [122]. The project includes developing a solar reforming reactor with associated heat exchangers, which has already been observed to convert concentrated solar energy into chemical energy with a high efficiency. The work is part of DOE funded project and the author claims that – because the development and commercialization path to this system is relatively short – it can be commercialized and in operation at multiple locations before the year 2020.

Nevertheless, it is highly probable that large scale solar thermal reforming will require the economies of scale offered by heliostat fields with central tower receivers. These fields can comfortably generate solar thermal fluxes in the MW capacity, although the deployment of such fields to date has been limited to electricity generation.

The technology of choice will be one which can be deployed cost effectively at large scale. The choice of directly-irradiated volumetric receivers versus cavity (tubular) indirectly irradiated ones for solar-driven catalytic reactions will be a key decision in technology development. Volumetric absorbers appear to offer better thermal and performance properties than conventional tubular ones, the convenience being based primarily on their intrinsic mechanism of light absorption, which is three-dimensional in nature. Directly irradiated reactors provide efficient radiation heat transfer directly to the reaction site where the energy is needed by-passing the limitations imposed by indirect heat transport via heat exchangers. Since solar energy is absorbed directly by the catalyst, temperatures are highest at the reaction sites and the chemical reactions are likely to be kinetically-limited rather than heat transfer-limited as in conventional tubular reactors. A further advantage is that the intensity of the impinging solar radiation can be five times higher than in a tubular receiver Fig. 4a [13]). The concurrent flow of solar radiation and chemical reactants reduces absorber temperatures and re-radiation losses.

The disadvantages or limitations of the DIVRR largely centre on the need to have a transparent quartz window as the aperture to allow the ingress of concentrated solar radiation into the receiver whilst at the same time providing a gas seal for the reacting gases and products that in most cases are under pressure. This window must at all times be kept cool and free from contact with any gases or solids within the receiver that could damage or destroy it by either increasing its opacity or reacting with it in some way. Methods such as protecting the window with a flow of inert auxiliary gas or by ensuring that the flow pattern of solids inside the receiver is such that they cannot contact the window have really only been partially successful to date and more work needs to be done on this crucial aspect before the quartz window can be considered to have the reliability needed for a commercial large-scale receiver.

Indirectly irradiated reactors eliminate the need for a window at the expense of having less efficient heat transfer – by conduction – through the walls of an opaque absorber. Thus, the disadvantages are linked to the limitations imposed by the materials of the absorber, with regard to maximum operating temperature, inertness to the chemical reaction, thermal conductivity, radiative absorbance, resistance to thermal shocks and suitability for transient operation.

Another set of issues relates to the choice of steam or CO_2 for reforming. There are advantages and disadvantages for each option with a clear choice only for certain open-cycle applications. For example, if methanol were the desired end-product, the amount of steam or CO_2 used would give an optimal CO/H_2 ratio in the syngas. If H_2 were the desired product, steam reforming is the choice. A process configuration considered more recently is the mixed reforming of methane, where it reacts with a mixture of water and CO_2. This process is especially advantageous for methane sources with a high CO_2 content such as biogas (45–70 mol% CH_4 and 30–45 mol% CO_2). These feedstocks often contain close to the required CO_2 amount for the reforming reaction and only a small amount of steam needs to be added, which also reduces carbon formation. Furthermore, the resulting H_2/CO ratio in the product can be adjusted (by the amount of steam added), according to the requirements of further processing. For the

utilization of biogas this constitutes an attractive possibility for upgrading the heating value. That way, combustion difficulties with biogas at low engine loads can be reduced [35,123–126].

Even though it is generally accepted that with current investment costs all CSP-aided solar fuels production technologies do require a public support strategy for their deployment into the market [127], one of the major obstacles to their commercialization is the lack of long-term, committed, industrial financial support. Such a support is necessary for not only the initial erection but especially the long-term operation of a demonstration plant that will help in identifying particular technology advantages as well as drawbacks. At least up until now, technologies that have reached the status of solar platform-scale tests have done so through the financial support of EU- or national governments-funded projects; however due to time limitations in most of the cases specific subcomponents of a full solar plant are tested and validated and not the integrated process as a whole. On the other hand the often intermittent nature of this funding, results in stalling of the development endeavour before reaching the status of e.g. an automated process, producing long-term experimental results. In this perspective, perhaps “technically simpler” concepts like, for instance, the tubular indirectly-heated (“alllothermal”) reformers employed in the ASTERIX project, might be more attractive for large-scale implementation and demonstration of the technology.

In conclusion, significant progress has been made through the research efforts described above and the solar driven steam reforming of methane has been demonstrated at pilot scale. The technologies for both DIVRR and tubular reactors are both ready for small commercial scale installations, and it is anticipated that plants in the 1–5 MW_{th} region will be constructed in Australia and Europe within the next couple of years. The transitional nature of this technology – coupling renewable solar thermal energy and conventional fossil fuels to make either a synthesis gas or hydrogen – is seen as a key first step on the path to sustainable hydrogen and energy production.

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